

Theoretical study of the dissolution of copper from chalcopyrite

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Declaration of Originality

I hereby declare that the research presented in this thesis is my own. It has not been submitted in any form for another degree or academic qualification at any university or institution of higher education. Information derived from any internet sources, books, and published or unpublished work of others has been acknowledged in the text and a list of references is given in the bibliography. Any additional sources of information have been appropriately referenced. The research presented in this thesis was conducted under the supervision and guidance of Doctor Patricia A. Hunt and Professor Nicholas M. Harrison at Imperial College London in South Kensington.

Vincent Huair-Yu Chen

September 2016

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Abstract

A lot is unknown about the chemical mechanisms relevant to the dissolution of Cu from CuFeS₂. This is a severe problem in the context of hydrometallurgical extraction, as it is currently not possible to obtain economical Cu yields from CuFeS₂ mineral.

In this work, periodic hybrid-exchange density functional calculations have been performed on CuFeS₂ bulk and slabs representing various surface orientations. In the bulk study, geometric, electronic and magnetic properties of the ground state have been obtained and compared with experiment to validate the density functional methodology. In addition, the bonding properties of CuFeS₂ have been studied, leading to the conclusion that CuFeS₂ is semi-ionic.

From the slab calculations, the surface energetics have been used to predict the surface morphology of CuFeS₂, and hence the surface orientations likely to be exposed upon cleavage. In particular, the polar (112)/($\overline{1}\overline{1}\overline{2}$) surface pair featured heavily in the predicted equilibrium crystallites due to its remarkably low surface energy. The stability of the surface pair was attributed to a combination of geometric and electronic stabilisation mechanisms.

In the final part of this work, an attempt was made to develop a QM/MM embedded cluster methodology for the purpose of studying Cu dissolution mechanisms. The methodology was benchmarked against the periodic QM methodology employed in the study of CuFeS₂ bulk and surfaces. The embedded cluster methodology was in general able to accurately reproduce the periodic QM electronic structure. However, the potential energy surfaces and optimised geometries predicted by the embedded cluster methodology differed significantly to those obtained from periodic slab calculations. The developed methodology was therefore deemed to be unsuitable for further study; this is likely due to the inability of the embedding charges to robustly model long range electrostatic interactions.

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1

Introduction

1.1 Core motivation: Copper extraction

Copper was the first metal to be used by man with archaeological evidence suggesting that the Sumerians and ancient Egyptians were its first widespread users more than 6000 years ago [4]. Since then, copper has played an important role in human civilisation owing to its numerous useful properties. The ductility of copper induced the ancient Egyptians to use it for water piping. Around 3000 BC, the discovery of bronze, an alloy of copper with tin, led to the Bronze age, during which various tools, weapons, armours and building materials far more durable than their stone-based counterparts were developed. In the Middle Ages, the anti-corrosion properties of copper led to its architectural use as roof sheathing for many important buildings such as the Pantheon and the Hildesheim Cathedral. The discovery of electricity and magnetism and the manufacturing of stable and highly conductive electrical wiring in addition to other products that used copper helped launched the Industrial Revolution.

Copper is characterised by its unique set of chemical (corrosion and bacteria resistant), mechanical (malleable, ductile and high tensile strength) and physical (strong heat and electrical conductivity) properties that makes it superior with respect to most materials used as substitutes. For example, aluminium can replace copper in electrical cables. However, its lower conductivity means that a larger amount of the metal is required for a fixed length of cable compared to copper. Another example is plastics, which can replace copper in water piping and other plumbing fixtures. However, unlike copper, plastics can burn and generally do not have the chemical properties to protect water systems from harmful bacteria.

In addition to its unique properties, copper is also one of the more abundant metals

on Earth, with an estimated atom-abundance of 68 parts per million (ppm) in the continental crust [5]. While not as abundant as iron (63,000 ppm) and aluminium (82,000 ppm), copper is more abundant than other industrial metals such as lead (10 ppm) and tin (2.2 ppm), and significantly more abundant than silver (0.08 ppm) and gold (0.003 ppm) [5]. Consequently, copper is one of the most heavily used metals today and is essential to achieve a good standard of living in modern life. In the construction industry, copper is used in electrical wiring, plumbing and heating, gutters, and roof and wall cladding. In the electrical and electronics industry, copper has important applications in telecommunications, power utilities, industrial controls and lighting. Copper is also used in various parts on all modes of modern transportation, and in consumer goods such as appliances, cooking utensils, jewellery and art.

World economic growth, currently driven by developing countries such as China and India is heavily dependent upon the availability of copper and other raw materials. The global usage for copper, shown in Figure 1.1, has therefore increased exponentially over time and is unlikely to subside in the near future. Geologically, copper can be found in a variety of sulphide, oxide and silicate ores, but the mineral chalcopyrite (CuFeS_2) alone accounts for the majority ($\sim 70\%$) of copper reserves on Earth [6, 7].

Currently, 80-85% of refined copper, defined in the Harmonised System as metal containing at least 99.85% copper by weight, is obtained by pyrometallurgical processing of ore concentrates [8]. This involves the use of high temperature chemical reactions in processes such as roasting, smelting and converting. Environmentally, these processes lead to the emission of sulphur dioxide gas, which is linked to visibility degradation and acid rain. Furthermore, leakage of waste products such as heavy metals and acidic discharge can contaminate the surroundings and pose significant health risks. Due to the energy requirements of the high-temperature processes as well as additional costs associated with mitigating negative environmental impact, the ore grade, which refers to the concentration of the desired metal in the mineral, is a key factor which determines the economically viability of pyrometallurgical treatment.

With the preferential processing of high grade ores, the average copper ore grades of deposits have declined over time despite the occasional discovery of high grade deposits, as illustrated in Figure 1.2. As a consequence, the proportion of ore of which pyrometallurgical processing is not economically justified has continued to increase. This necessitates the application of alternative extractive methods to satisfy global demands for copper. Hydrometallurgy, which involves the use of solution chemistry, is currently the alternative extractive route for processing copper ore and is also used to further extract metal from unused ore of pyrometallurgical processes. A key tech-

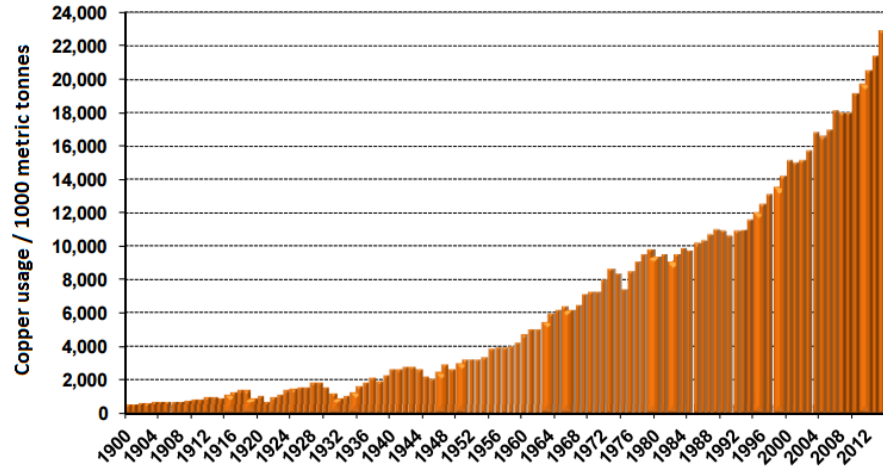


Figure 1.1: World refined copper usage from 1900 to 2014. Graph taken from The World Copper Factbook 2015 published by the International Copper Study Group.

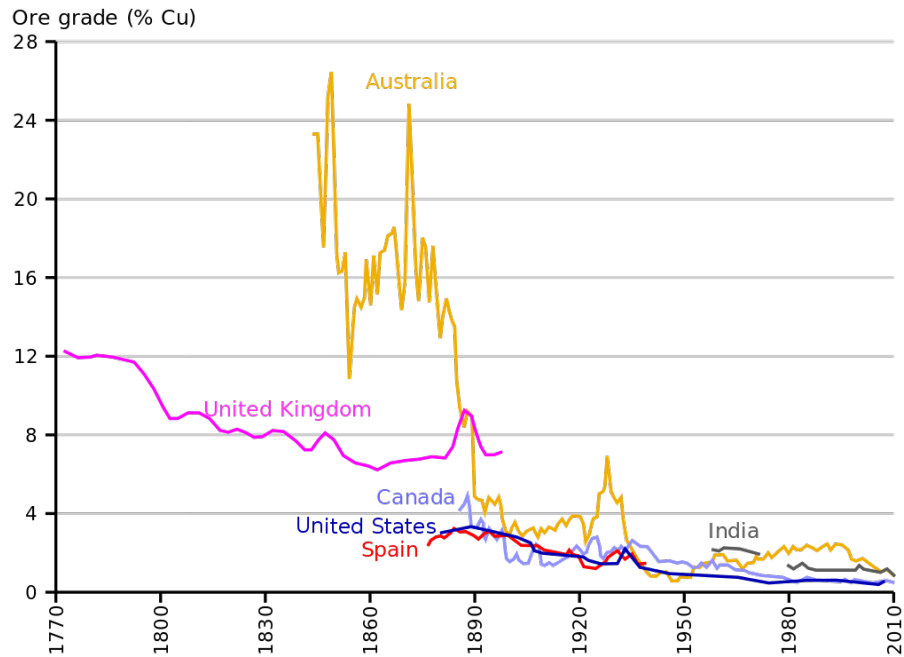


Figure 1.2: Average grades of copper ores in several global locations from 1770 to 2010. © User:Bovran53 / Wikimedia Commons / CC-BY-SA-4.0

Time required	Mineral	Ideal formula
Hours to days	Atacamite	$\text{Cu}_2\text{Cl}(\text{OH})_3$
	Chrysocolla	$\text{CuSiO}_3 \cdot 2\text{H}_2\text{O}$
	Neotocite	$(\text{Cu}, \text{Mn})_2\text{H}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot n\text{H}_2\text{O}$
	Tenorite	CuO
	Malachite	$\text{Cu}_2(\text{CO}_3)(\text{OH})_2$
	Azurite	$\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$
	Antlerite	$\text{CuSO}_4 \cdot 2\text{Cu}(\text{OH})_2$
	Brochantite	$\text{CuSO}_4 \cdot 3\text{Cu}(\text{OH})_2$
Days to month	Native Cu	Cu
	Cuprite	Cu_2O
	Chalcocite	Cu_2S
Months to years	Bornite	Cu_5FeS_4
	Covellite	CuS
	Enargite	Cu_3AsS_4
	Chalcopyrite	CuFeS_2

Table 1.1: Comparative dissolution rates in laboratory-scale tests using acidic sulphate systems for different copper-bearing minerals found in heaps and dumps of low-grade ores [2].

nique of hydrometallurgical extraction, is leaching, which involves the percolating of a solution, called the leachate, through crushed ore to dissolve the mineral. The desired metal is then recovered through iron precipitation or solvent extraction. Unlike pyrometallurgical methods, hydrometallurgical processing is justified for low-grade ore due to its relatively low cost. Other advantages of hydrometallurgical processing include short construction times and minimal required supervision during operation. Moreover, hydrometallurgy is generally seen as more environmentally friendly compared to pyrometallurgy due to no sulphur dioxide emissions, though measures must be taken to prevent seepage of acidic leachates that could otherwise contaminate surface water and groundwater.

The main problem of hydrometallurgy in the context of copper extraction, is the severe refractory nature of CuFeS_2 ore. As seen in Table 1.1, in acidic sulphate media, commonly used for leaching, CuFeS_2 has one of the slowest dissolution rates out of copper-bearing minerals commonly found in heaps and dumps of low-grade ores. The inability of modern methods to significantly accelerate the slow leaching kinetics of CuFeS_2 means that hydrometallurgical treatment of the mineral is currently economically unfeasible due to unsatisfactory yields [7, 8]. It is well established that a passivation layer is to blame for the poor recovery rates, but despite extensive research

over the last few decades, there is no consensus on neither the identity of the passivating species nor details of associated leaching and passivating mechanisms [7]. One reason for the difficulty in elucidating fundamental surface properties of CuFeS_2 is the complexity of the leaching system due to the numerous competing surface phases that have been detected in various spectroscopic studies. Another reason is the fact that CuFeS_2 exhibits poor cleavage, in other words a variety of surfaces are exposed upon fracture, hence systematic study of leaching on specific surface orientation has thus far not been possible [8].

On the theoretical side, surface properties of CuFeS_2 have not received commensurate attention; only a limited number of theoretical studies have been published. Furthermore, CuFeS_2 is a semi-ionic material with strong on-site correlation due to the presence of open d -shell ions. It is therefore a material that standard density functional calculations with the local density approximation or generalised gradient approximation are unlikely to describe accurately. Hence, the few studies that have been conducted are of dubious accuracy.

A range of CuFeS_2 surface orientations have been studied theoretically but the properties investigated have been limited to surface reconstruction and electronic properties but not energetics. The surface morphology of CuFeS_2 , is hence currently not well understood. In addition, with the exception of a few adsorption studies of single molecules, there have been no relevant studies on the interaction between CuFeS_2 and the liquid phase. The lack of studies on systems which incorporate a full solid-liquid interface is due in part to the difficulty of *ab initio* methods in probing the molecular properties of liquids that contain a mixture of species. The limited scope of theoretical studies has meant that these have not provided considerable clarity with regards to CuFeS_2 chemistry.

1.2 Project strategy and thesis structure

This overall aim of this project was to fill the gap in the fundamental knowledge of CuFeS_2 surface reactivity in the context of copper dissolution through theoretical calculations. The first stage of the project was the study of fundamental bulk properties using *ab initio* calculations. As the bulk properties of CuFeS_2 are generally well understood from decades of research, one goal of the bulk calculations performed in this work was to validate the density functional methodology employed through comparison of calculated properties against established experimental counterparts. A few exceptions are the band gap and the valence state, both of which have been subject to debate. As

these two properties may play a key role in the reactivity of CuFeS_2 , another goal of the bulk calculations was to obtain an accurate evaluation of them.

The second stage of the project was the study of the surface properties of CuFeS_2 , also using *ab initio* calculations. One of the key aims of this stage was the identification of stable surface orientations that are likely to be exposed upon fracture. As there are an infinite number of possible surface orientations, a systematic approach based on Tasker's classifications was developed to filter down the number of surfaces to those likely to be stable, in other words those with a low surface formation energy. This provided a means to limit the overall computational cost. The formation energies as well as geometric and electronic properties were determined for the filtered set of surfaces. The surface energy data was used to predict equilibrium crystallite morphologies which in turn enabled deduction of the surfaces most likely to exist, and hence the surfaces that should be considered for subsequent study of copper dissolution.

The final part of this project was dedicated to the development and testing of a suitable methodology for the study of copper dissolution. As the study of reactivity at a solid-liquid interface requires a robust methodology that can achieve chemical accuracy in a large and complex environment, the hybrid Quantum Mechanics/Molecular Mechanics (QM/MM) approach was used as the basis for methodology development as it provides an appropriate compromise between computational cost and accuracy. As no MM force field exists for the CuFeS_2 system, an attempt was made to parameterise a suitable force field. Systematic testing was then performed on the developed methodology to assess its accuracy and ultimately determine its suitability for further study of dissolution.

The thesis is organised as follows. In Chapter 2, a review of the relevant literature is given. In Chapter 3, an overview of the theoretical methods utilised in this project is presented. In particular, classical MM, electronic structure methods and the hybrid QM/MM approach are described in detail. In Chapter 4, a hybrid-exchange density functional theory (DFT) study of the geometric, electronic and magnetic properties of bulk CuFeS_2 is presented. In particular, a detailed analysis of the nature of the bonding in CuFeS_2 is also given. In Chapter 5, a hybrid-exchange DFT study of the surface morphology of CuFeS_2 is presented with particular focus on the stability of the polar $(112)(\bar{1}\bar{1}\bar{2})$ surface pair. In Chapter 6, the development of a QM/MM methodology for study of CuFeS_2 dissolution is described and the results obtained from subsequent systematic testing of the methodology are presented. Finally, in Chapter 7, conclusions derived from this work are given along with a commentary of potential future work.

2

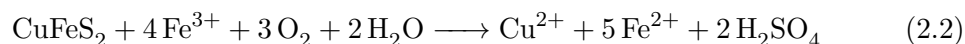
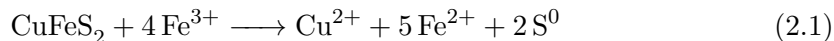
Review of Literature

This chapter provides a review of the literature relevant to this project, with particular focus on the bulk and surface properties of CuFeS_2 . In Section 2.1, a brief summary of the current understanding from recent experimental research is given to put the aims of this project into context. In Section 2.2, a review of previous experimental and theoretical studies of bulk CuFeS_2 is presented. In Section 2.3, an account of the current understanding on surface properties of CuFeS_2 in addition to the closely related CIGS $[\text{Cu}(\text{In,Ga})(\text{S,Se})_2]$ compounds is provided. Finally, a summary is given in Section 2.4.

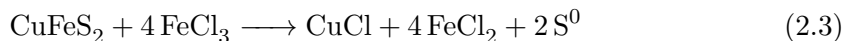
2.1 Experimental studies of Cu leaching from CuFeS_2

The term *oxidative leaching* is often used to refer to hydrometallurgical extraction of Cu from CuFeS_2 as it involves the oxidation of Cu(I) (in solid) to Cu(II) (in solution). Ferric ions (Fe^{3+}), from ferric sulphate $[\text{Fe}_2(\text{SO}_4)_3]$ or ferric chloride (FeCl_3) are most commonly used as oxidation agents [9–15]. Other reagents such as ozone [16], cupric $[\text{Cu}(\text{II})]$ ions [17, 18] and silver(I) ions [11] have also been trialled.

According to Dutrizac, the overall equations representing the dissolution of Cu from CuFeS_2 in the presence of Fe^{3+} ions are [19]:

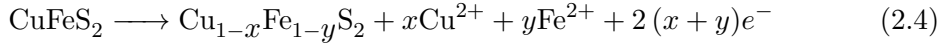


A third reaction was proposed by Haver and Wong to describe CuFeS_2 dissolution with FeCl_3 [20]:



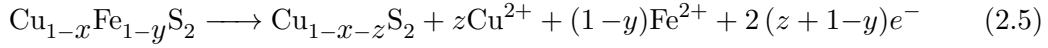
Spectroscopic surface analysis in leaching studies has revealed the presence of a host of compounds including jarosites [$X\text{Fe}_3(\text{SO}_4)_2(\text{OH}_6)$], iron oxides (Fe_xO_y) and hydroxides ($\text{Fe}_x\text{O}_y\text{OH}_z$), polysulfides ($X\text{S}_n$), and copper sulphides (Cu_xS_y) [14, 21–27]. These are often speculated to be the intermediate phases of reactions (2.1), (2.2) and (2.3). The resulting complexity of the system means that despite the efforts of many researchers, it has proven extremely difficult to deduce a comprehensive reaction model detailing the mechanisms of leaching accounting for all the species. Some of the proposed models are detailed as follows.

Hackl *et al.* proposed that a combination of chemical and diffusion control governed the leaching and passivation of CuFeS_2 in sulphate medium [12]. In their model, Fe dissolves preferentially over Cu which results in the formation of an intermediate disulphide phase:

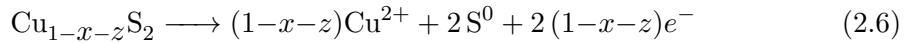


with $y > x$, $x+y \approx 1$.

This is followed by the dissolution of the disulphide to form a copper polysulphide:

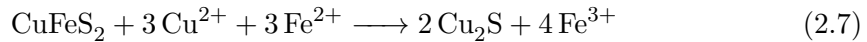


The copper polysulphide, $\text{Cu}_{1-x-y}\text{S}_2$, is proposed to be responsible for passivation with the rate-controlling step being the slow decomposition of polysulphide to Cu^{2+} ions:

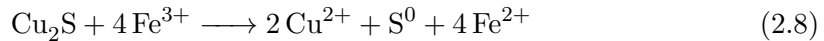


Porous elemental sulphur is produced from this step, and has no effect on CuFeS_2 passivation in this model.

The model proposed by Hiroyoshi *et al.* is based on observations that a narrow “potential window” exists for effective leaching of chalcopyrite [7, 28, 29]. The first step of the model is the incomplete reduction of chalcopyrite:

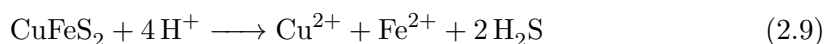


This is followed by the oxidation of covellite (Cu_2S) by Fe^{3+} ions:

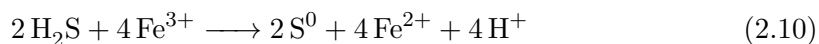


It was observed that reaction (2.7) is only feasible below a critical potential. This provides an explanation for the decreased dissolution rate observed at high potentials and implies that the ratio of Fe³⁺/Fe²⁺ therefore strongly influences the kinetics. Note that the sum of reactions (2.7) and (2.8) gives the reaction (2.1).

Nicol and Lazaro proposed a model to explain leaching at redox potentials less than 0.4 V [30]. The first stage is the reduction of chalcopyrite by protons:

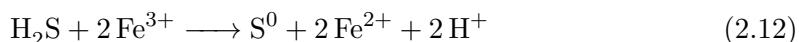
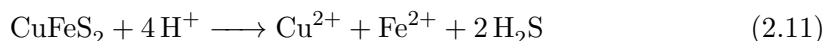


This is followed by the oxidation of hydrogen sulphide by Fe³⁺:

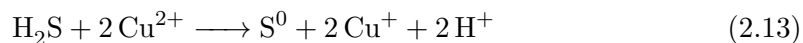


In this model the rate-controlling step is electrochemical; when the redox potential of CuFeS₂ surface increases from 0.5 to 0.7 V, the rate of the reaction (2.10) decreases.

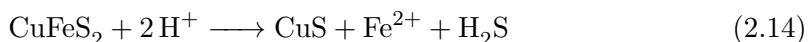
The model proposed by Yelásquez-Yévenes and co-workers is based on leaching experiments in dilute chloride solutions under controlled potentials that found an enhanced dissolution rate for solution redox potential in the range of 550 to 600 mV vs. standard hydrogen electrode (SHE) [31–33]. Two mechanisms were derived, both involving a non-oxidative step under acidic conditions, followed by an oxidative step. The first mechanism is as follows:



OR



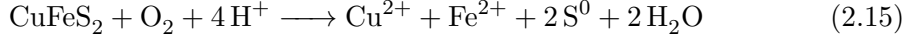
Yelásquez-Yévenes and co-workers suggested that the H₂S oxidation was faster with Cu²⁺ ions than with Fe³⁺; this explains the faster kinetics observed in chloride media compared to sulphate media. The second mechanism is:



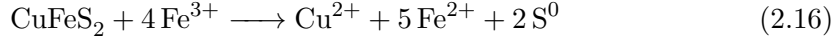
This is followed by oxidation by ferric ions [reaction (2.12)] or cupric ions [reac-

tion (2.13)] and oxidative leaching of the intermediate CuS. This mechanism is supported by the observation of CuS in leaching samples.

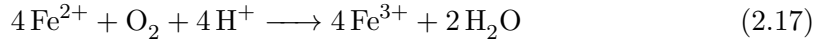
Ruiz *et al.* proposed that in acidic aqueous solutions, the dissolution of CuFeS₂ with oxygen can be represented by [34]:



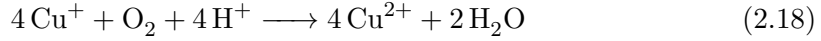
The ferrous ions produced can be oxidised to ferric ions, which themselves can oxidise CuFeS₂ according to the following reaction:



The Fe³⁺ ions are regenerated as follows:



The combination of reactions (2.16) and (2.17) gives the overall leaching reaction (2.15). Here, the redox couple is the Fe³⁺/Fe²⁺ pair. When Cl⁻ is present in the leaching solution, the Cu²⁺/Cu⁺ redox couple can also be operative according to the following reactions [35]:



Leaching of CuFeS₂ by Cu²⁺ can occur because of the greater stability of the chloro-complexes of Cu⁺ compared to the chloro-complexes of Cu²⁺ [35]. Like Fe³⁺ ions, Cu²⁺ ions can be regenerated by oxygen. It has been observed that the regeneration of Cu²⁺ is more efficient compared to Fe³⁺ at atmospheric pressure [36, 37].

Klauber proposed a general, conceptual 4-stage dissolution model to account for leaching kinetics as well as residues [38]. In the initial stages, a thin layer of elemental sulphur forms on the surface and acts as a diffusion layer. At a later stage, jarosites form at the surface and cause passivation.

Leaching conditions, which covers factors such as temperature, pH, redox potential and the concentration of various species, have been shown to play a huge role in the dissolution rate. The effect of several commonly investigated factors on Cu dissolution are briefly described below.

Temperature. It has been shown in many studies that the rate of leaching increases significantly with temperature with no negative consequences on the final copper yield [39–44]. Calculated activation energies are high (>50 kJ/mol) regardless of the leaching

medium, again implying that higher temperatures are more favourable for leaching. While this information may not be directly applicable in the context of heap leaching where temperatures are unlikely to be above 25°C, it may give valuable insight into the nature of the rate limiting processes [40].

pH. The acidity of the system is influential as it dictates the composition of the leaching solution. For example, the logarithmic constant (pK_a) of H₂SO₄ is 1.9 at room temperature which implies that when the pH is above 1.9 the predominant species is SO₄²⁻, while at lower pH values the predominant species is HSO₄⁻. Most studies show that an acidic, but not too acidic environment favours leaching. Diminished dissolution rates at sufficiently low pH values have been reported by several authors [13, 43]. Córdoba et al. (2008) reported an optimal copper yield at a pH of around 2 [7].

Ferric ion concentration. Several studies suggested that the Cu dissolution rate improves with Fe³⁺ ion concentration, but only up to a limiting concentration that ranges from between 0.01 M and 0.1 M. Ruiz *et al.* reported a reduction in the leaching rate when the Fe³⁺ ion concentration was increased from 0.0036 M to 0.055 M [34]. Results from a recent study suggest that the presence of Fe³⁺ as opposed to Fe²⁺ gives a higher initial rate of Cu dissolution but also facilitates passivation [45].

It is generally accepted that the main cause of slow dissolution kinetics is the formation of a passivation layer on the mineral surface, though the species that causes this refractory behaviour is still under debate. A variety of candidates have been proposed to be the cause of passivation. These include elemental sulphur, jarosites, metal-deficient sulfides and polysulfides [7,9,12,38]. However, despite decades of experimental research, there is no consensus on either the identity of passivating species or the mechanism of rate limiting step.

2.2 Properties of bulk CuFeS₂

As well as being a highly abundant mineral, CuFeS₂ was also one of the earliest known semiconductors. As a consequence, CuFeS₂ was one of the first materials used in radio wave detectors and since the 1950s has been the subject of a significant body of research carried out to understand its properties [46]. This section will summarise some of the key findings from experimental and theoretical studies of bulk CuFeS₂.

2.2.1 Structure properties

Burdick and Ellis were the first to report the crystal structure of CuFeS_2 in 1917 [47]. However, the cubic structure that they proposed from X-ray diffraction was proven to be incorrect. Pauling and Brockway gave the first correct description of the structure of CuFeS_2 via X-ray diffraction in 1932 [48]. They characterised the structure of CuFeS_2 as a tetragonal lattice with space group $I\bar{4}2d$.

The conventional unit cell of CuFeS_2 is akin to that of sphalerite (zinc-blende) except doubled in the crystallographic c direction and consists of corner sharing MS_4 tetrahedra as depicted in Figure 2.1. The cationic sublattice has an ordered arrangement such that each metal atom is coordinated to four sulphur atoms, while each sulphur atom is coordinated to two copper and two iron atoms. In addition, the atomic layers parallel to the crystallographic a - b plane alternate between being composed of only metal species and only sulphur. The lattice parameters and other structural parameters of CuFeS_2 have since been estimated in a range of studies using X-ray and neutron diffraction [49–52].

The first reported theoretical study of CuFeS_2 was in 1974 by Kambara, who used the extended Wolfsburg-Helmholtz method, a semi-empirical molecular orbital method, to study the electronic states of CuFeS_2 [53]. However, due to the lack of computational power, the system studied was limited to a small finite cluster consisting of only 17 atoms, thus they were not able to study the crystal structure. With the increasing accessibility of computational methods, several density functional theory (DFT) studies have been performed in the last few decades utilising periodic boundary conditions (PBC) to study bulk CuFeS_2 .

A summary of the lattice constants and other structural parameters obtained from experimental and theoretical studies is presented in Table 2.1. The experimental data exhibits great consistency; the difference between the maximum and minimum lattice constants and bond lengths is around 1%. The presence of 2 rather 1 cationic species means that the unit cell is slightly distorted compared to a doubled sphalerite cell, giving a c/a ratio of just under 2. On the contrary, there is far less consistency in the theoretical data with a range of around 7% in the calculated lattice constants. This indicates that the results are highly sensitive to the method used.

In the DFT study of bulk CuFeS_2 by Zhou *et al.*, the VWN functional, based on the local density approximation (LDA) and the PBE functional, based on the generalised gradient approximation (GGA), were used, with and without the Hubbard U correction for on-site interactions [54]. The VWN and PBE functional both considerably under-

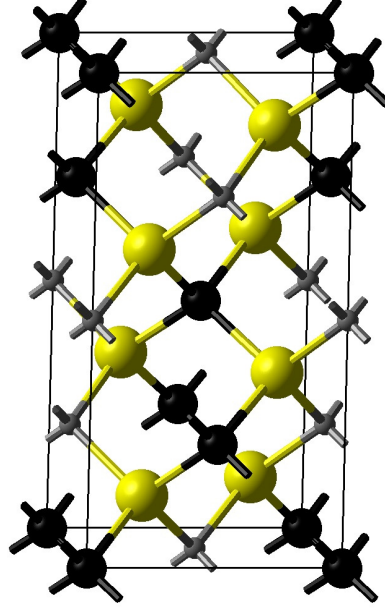


Figure 2.1: Conventional unit cell of bulk CuFeS_2 . Copper, iron and sulphur atoms are coloured black, silver and yellow respectively.

estimated the lattice constants. The inability of neither LDA nor GGA to capture the correct physics of strongly correlated materials is reflected in the structure predictions. With the inclusion of the Hubbard U parameter for Fe species whose value was optimised to lattice parameters and band gap, there is significant improvement in the predicted lattice constants, although LDA+ U still significantly overbinds the crystal. The GGA-PW91 functional has been shown to accurately reproduce the experimental lattice constants [3, 55].

2.2.2 Electronic and magnetic properties

The electronic and magnetic structure of CuFeS_2 has also been investigated in numerous studies. In 1954, Goodman and co-workers first suggested a band gap of at least 0.5 eV based on the information that CuFeS_2 shows point-contact rectification and transmits infrared radiation at wavelengths longer than $2\ \mu\text{m}$ [57]. In later experimental studies, band gaps of 0.53, 2.6 and 0.6 eV have been determined on naturally occurring CuFeS_2 samples from infrared measurements [58], the four point method for electric conductivity [59] and optical measurements [56], respectively. In addition, a value of 0.575 eV was obtained via optical measurements performed on CuFeS_2 thin films grown from the sulphurisation of CuFe alloy precursors [60].

2. REVIEW OF LITERATURE

Method	a	c	c/a	u	$d_{\text{Cu-S}}$	$d_{\text{Fe-S}}$	Ref.	Notes
Experimental								
XRD	5.24	10.39	1.97	0.27	2.32	2.20	[48]	Joplin crystal Ugo crystal
XRD	5.24	10.34	1.97				[51]	
XRD	5.32	10.45	1.96				[51]	
XRD	5.289	10.423	1.97	0.257	2.302	2.257	[49]	
XRD	5.291	10.422	1.97				[56]	
XRD	5.286	10.410	1.97	0.256	2.299	2.256	[50]	
ND	5.280	10.430	1.98				[52]	
Avg.	5.28	10.40	1.97					
Theoretical (DFT with PPWP approach)								
PW91	5.265	10.534	2.00	0.258	2.305	2.256	[3]	$U_{\text{eff}}^{\text{Fe}} = 3 \text{ eV}$
PW91	5.263	10.362	1.97	0.2585	2.293	2.241	[55]	
LDA	4.955	9.851	1.99				[54]	
PBE	5.080	10.003	1.97				[54]	
LDA+ U	5.141	10.031	1.95				[54]	
PBE+ U	5.315	10.424	1.96				[54]	

Table 2.1: Structural parameters reported in previous experimental and theoretical studies. XRD = X-ray diffraction; ND = Neutral diffraction; PPWP = Plane-wave pseudopotential.

On the theoretical side, Hamajima *et al.* deduced a band gap of 0.3 eV using a discrete-variational $X\alpha$ (DV- $X\alpha$) technique [61]. A wide range of band gap values are predicted from recent DFT studies. The LDA study by Edelbro *et al.* predicts CuFeS_2 to be conducting [62] while the PW91 (GGA) functional predicts a small indirect gap of 0.1 eV [55]. Conejeros *et al.* [63], and Zhou *et al.* [54] employed the PBE (GGA) functional in addition to a Hubbard U correction term for Fe and reported band gap values of 0.55 and 0.94 eV respectively. The disagreement in their calculated values could be due to the different $U_{\text{eff}} (=U-J)$ parameter used (4.3 eV vs. 3 eV). Conejeros *et al.* also employed the hybrid-exchange functional B3LYP in their study, and obtained a band gap of 1.82 eV [63].

Due to the large range in both measured and calculated band gaps in addition to the limited number of samples, it is difficult to assess their reliability of the reported band gaps, hence the true band gap cannot be confidently stated. On the experimental side, it has been suggested that the variation in measured band gaps might be due to imperfections in the naturally occurring samples or pressure induced lattice modifications [62]. It is also possible that the value of 2.6 eV determined from electric conductivity using the four point method is unreliable given the relative consistency of

the other measured band gaps. On the theoretical side, it is clear that the band gap, like the structural parameters, is extremely sensitive to the method used. It should be noted that the DFT band gaps are consistent with the general trend that LDA and GGA underestimate the real band gap while B3LYP reliably reproduces the band gap in semiconductors, sulfides and ionic transition metal oxides [64].

The antiferromagnetic nature of CuFeS₂ was first conclusively determined in 1958 by Donnay *et al.* using the Gouy method along with analysis of powder neutron diffraction patterns [51]. In this magnetic configuration Fe spins are aligned within the crystallographic *a-b* plane and alternate along successive planes along the [001] (crystallographic *c*) direction, as shown in Figure 2.2 [51]. It has been determined in subsequent neutron diffraction studies that this antiferromagnetic configuration is the magnetic ground state of CuFeS₂ between 50 and 750 K [52,65].

In addition to the magnetic ground state, Donnay *et al.* also deduced that the magnetic moment is 3.85 μ_B for Fe and has a maximum of 0.2 μ_B for Cu. More recent experimental studies give varying values for the magnetic moments. Fujisawa *et al.* utilised a range of electron and optical spectroscopic techniques and obtained a value of 3.8 $\pm$ 0.1 μ_B for Fe. The neutron diffraction study performed by Woolley *et al.* on powdered polycrystalline CuFeS₂ gave moments of 3.42 $\pm$ 0.07 μ_B and $\sim$ 0.05 μ_B for Fe and Cu respectively while another neutron diffraction study performed by Engin *et al.* gave a value of 3.67 $\pm$ 0.05 μ_B for Fe.

The effectively zero magnetic moment suggests that Cu is monovalent (Cu⁺), which in turn implies a formal valence state of Cu⁺Fe³⁺(S²⁻)₂, rather than Cu²⁺Fe²⁺(S²⁻)₂. However, the measured magnetic moment for Fe is substantially lower than what is expected for an isolated high-spin trivalent Fe³⁺ ion (*d*⁵; $\mu_B = 5.0$). This has led to significant debate on the reason for the discrepancy between the valence state and measured magnetic moments.

The valence state was initially proposed to fluctuate between Cu⁺Fe³⁺(S²⁻)₂ and Cu²⁺Fe²⁺(S²⁻)₂ from comparison of measured bond distances with known ionic radii [48]. Hall and Stewart later noted that while the bond distances are more compatible with Cu²⁺Fe²⁺(S²⁻)₂, the tetrahedral co-ordination of Cu suggests that it is in the Cu⁺ valence as Cu²⁺ usually coordinates in octahedral or square planar configuration. In addition, the fact that the measured Fe-S-Fe angle (110.70°) was only slightly greater than that in a perfect tetrahedral system (109.47°) was used to justify that superexchange interactions did not play a significant role, as in such a situation iron atoms would attempt to subtend an angle of 180° to minimise the associated energy. Hall and Stewart therefore concluded that CuFeS₂ has strongly covalent bonding with an

effective ionic state between $\text{Cu}^+\text{Fe}^{3+}(\text{S}^{2-})_2$ and $\text{Cu}^{2+}\text{Fe}^{2+}(\text{S}^{2-})_2$.

The mixed valence model has however been since disputed in many spectroscopic studies, as in general the lack of complex hyperfine features or much broader lines in spectra indicate a single valence state [59, 66–69]. In particular, Boekema and co-workers suggested that mixed valence behaviour observed in earlier studies may indicate ill-defined samples, as seen in their study of ruthenocuprates [68, 70].

A few studies have proposed the $\text{Cu}^{2+}\text{Fe}^{2+}(\text{S}^{2-})_2$ state based on X-ray absorption spectroscopic (XAS) evidence [71, 72]. However, the majority of recent studies, which have employed a range of techniques including Mössbauer effect spectroscopy (MES) and X-ray photoelectron spectroscopy (XPS) in addition to XAS support the $\text{Cu}^+\text{Fe}^{3+}(\text{S}^{2-})_2$ state [65–69, 73]. In most of these studies, the lower than expected magnetic moment of Fe has been attributed to significant covalent interactions between Fe and S. With regards to XAS evidence of the $\text{Cu}^{2+}\text{Fe}^{2+}(\text{S}_2)^{2-}$, Pearce *et al.* pointed out that it is rare that XAS provides immediate verification of the valency state and hence complementary spectroscopic techniques such as MES and XPS are necessary [69].

On the theoretical side, the antiferromagnetic ground state has been reproduced in all reported studies. In addition, the calculated magnetic moment is also observed to be zero for Cu. For Fe, the calculated magnetic moment varies depending on the method used, but is generally consistent with the experimental values. Hamajima *et al.*, who performed band structure calculations using the discrete-variational $X\alpha$ method, obtained a value of $3.88 \mu_B$ [61]. In addition, they concluded that the low Fe magnetic moment is due to delocalisation of the minority spin *d*-electrons that are found to mix strongly into the upper-valence bands. Fe magnetic moments derived from DFT calculations range between 3.08 and 3.93 [3, 54, 55, 62, 63]. Strong covalent interactions between Fe-S are also concluded through analysis of Mulliken overlap populations [54], electronic density of states [62] and phonon density of states [3]. This is consistent with the majority of experimental results.

2.3 Studies of the surfaces of CuFeS_2 and related compounds

2.3.1 Experimental studies of CuFeS_2 surfaces

A significant amount of research has been dedicated to the study of CuFeS_2 surfaces. The majority of studies are experimental with the goal of identifying leaching intermediates and products on the mineral surface to determine relevant chemical mechanisms.

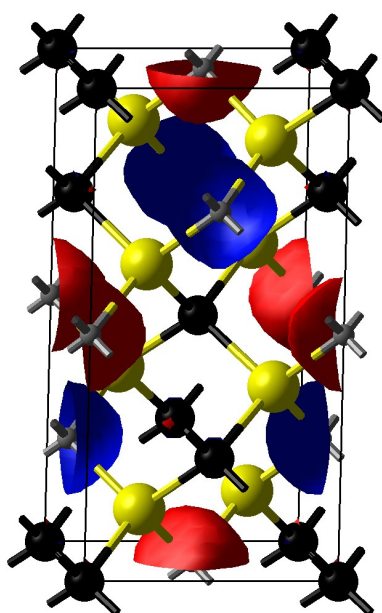


Figure 2.2: Conventional unit cell of CuFeS_2 with copper, iron and sulphur atoms coloured black, silver and yellow respectively. Red and blue spin density isosurfaces are plotted at isovalues of $+0.005$ and $-0.005 \mu_B/\text{\AA}^3$ respectively. This shows the antiferromagnetic nature of the ground state electronic structure.

However, this has proven to be an extremely difficult task due to several complications. First, significant variation in the purity of natural mineral systems means that the preparation of a model surface that is representative of the exposed mineral under realistic leaching conditions is impossible. Second, CuFeS_2 exhibits poor cleavage which means a range of surfaces are exposed upon fracture [74]. It is therefore difficult to reliably expose a certain surface for systematic study. Third, a large number of species such as elemental sulphur, metal deficient sulphides and jarosites have been identified at the CuFeS_2 surface [9, 12, 75, 76] while the leaching solution also contains a host of species including chlorides, sulphates, ferric and ferrous ions, and hydronium ions.

The rich mixture of species within the leaching system means that it is extremely complicated with a large number of interactions that may influence the rate limiting step for dissolution. This is reflected in the numerous possible leaching and passivation mechanisms that have been proposed. Fourth, as discussed in Section 2.1, many variables, including temperature, pH and concentration of various species in the leachate, have all been shown to affect the leaching kinetics. It is therefore not surprising that despite decades of intensive research, there remains considerable uncertainty regarding the surface chemistry of chalcopyrite in a leaching context. Nevertheless, some key information has been deduced from experimental as well as theoretical studies.

In experimental studies, XPS is commonly used to characterise the mineral surface as it can provide information about surface elemental composition, as well as the chemical and electronic states of the elements, hence allowing the surface speciation to be deduced.

Klauber used XPS to study CuFeS_2 surfaces polished in inert atmosphere [77]. It was concluded from the obtained spectra that a prominent component in the S 2p peak can only be attributed to the presence of the sulphide dimer S_2^{2-} . Based on this information, Klauber proposed that a stable layer of pyritic (FeS_2) composition and with 50% of the bulk density forms at the surface via a redox reconstruction mechanism following fracture. Klauber also speculated that this reconstruction mechanism is more likely to occur along (101), (110) and {001} planes due to their stepped nature, as opposed to the smoothly structured surfaces such as {112} planes. This implied that in the context of leaching chemistry, the (101), (110) and {001} surfaces are expected to be more reactive than the {112} surface.

Harmer also studied CuFeS_2 surfaces from untreated samples using XPS and deduced the presence of surface monomeric (S^{2-}) and polymeric (S_n^{2-}) sulphur species [78]. It was concluded that monomeric species form at nonpolar surfaces which have a mixture of metal and sulphur in the surface layer [e.g. (110)] while polymeric species

form at S-terminated surfaces [e.g. $(\bar{1}\bar{1}2)$]. For the latter, it was also suggested that S-polymeric species preferably form over Cu sites rather than Fe as Cu is more chalcophilic (attracted to S). Consequently, it is likely that in such surfaces Cu atoms are sterically hindered from oxidative dissolution, implying that exposed Fe should dissolve before Cu. This is supported by experimental observations of the preferential dissolution of Fe in the initial stages of leaching [12, 79].

Other experimental studies have employed a wide range of spectroscopic techniques to analyse the mineral surface [76, 80–83]. X-ray based techniques such as XAS, X-ray diffraction (XRD), X-ray emission spectroscopy (XES) and near edge X-ray absorption fine structure (NEXAFS) are used for surface characterisation and to deduce elemental and chemical composition across different depth regions. NEXAFS also provides information about formal valences and local coordination environment. Techniques that involve the use of electron or ion beams such as Auger electron spectroscopy (AES), scanning electron microscopy (SEM) and time-of-flight secondary ion mass spectroscopy (ToF-SIMS) can provide high resolution chemical images of surfaces and allow determination of the surface composition. Voltammetric methods such as linear sweep voltammetry and cyclic voltammetry are sometimes used in conjunction with surface analysis techniques to vary the electrochemical potential and hence simulate different electrochemical environments. The combined information obtained from the use of different techniques has led to the proposal of various dissolution and passivation mechanisms, some of which have been mentioned in Section 2.1.

2.3.2 Theoretical studies of CuFeS_2 surfaces

Due to the fact there have been very few studies on surfaces prior to deliberate leaching, in addition to the limitations in the techniques used, experimental studies thus far have not been able to deduce fundamental surface properties such as the geometric and electronic structure leading to poor understanding of the initial reactivity of CuFeS_2 . More recently, several theoretical studies have been conducted to fill this knowledge gap.

Von Oertzen *et al.* were the first to perform theoretical calculations on CuFeS_2 surfaces [84]. They performed density functional calculations using the PBE functional to study the nonpolar (012) surface and the polar (112) and $(\bar{1}\bar{1}2)$ surfaces. The (012) surface was concluded to be extremely unstable with an asymmetrical irregular structure with exposed S atoms following geometry optimisation. The metal-terminated (112) surface underwent significant geometric rearrangement during optimisation in

which surface metal atoms relaxed into the bulk, exposing sub-surface S atoms. This was in contrast to the S-terminated ($\overline{112}$) surface on which little relaxation occurred except for the formation of polymer S-chains at the surface. In addition, the Mulliken charges of S atoms in polymer chains were less negative compared to those in bulk CuFeS_2 , consistent with XPS results [78].

De Oliveira *et al.* studied the reconstruction of the S- and metal-terminated (001) surfaces using DFT with the PW91 functional [55]. At the metal-terminated surface, significant reconstruction occurred in which the surface metal atoms relaxed into the bulk, exposing S atoms at the surface and leading to the formation of a subsurface metal-alloy region with metal-metal bond lengths consistent with corresponding bulk metal. In contrast, the S-terminated surface underwent relatively little relaxation. The formation of S-S bonds was observed at both surfaces with bond lengths consistent with the disulphide anion (S_2^{2-}), implying oxidation of surface S species. From analysis of the electronic density of states (DOS), it was deduced that the oxidation of S was coupled with the reduction of surface Fe^{3+} to Fe^{2+} . This was consistent with observations from the XPS study by Harmer *et al.* [78]. De Oliveira *et al.* concluded that the reconstruction of the surface clearly influences surface reactivity in leaching. In particular, the occupation of 3d-Fe electronic states with antibonding character explains experimental observations that Fe dissolves before Cu.

In a subsequent study, de Oliveira *et al.* studied several other CuFeS_2 surfaces in addition to the (001) surface: the nonpolar (110), (102) and (114) surfaces, and the polar (100) and (112) surfaces [85]. The slab model was employed but only one surface was allowed to relax at a time. Three reconstruction mechanisms were identified from the study. The first mechanism, which applies to S-terminated nonpolar surfaces, involves the formation of surface S-S bonds to form S_2^{2-} coupled with the reduction of Fe^{3+} to Fe^{2+} . The (114) surface also reconstructs via this mechanism, but instead forms a S_4^{2-} chain at the surface. The second mechanism, which applies to metal-terminated nonpolar surfaces, involves the formation of alloy-like structures following the inward relaxation of surface metal atoms. This results in the exposure of S atoms originally in the subsurface atomic layer. The third mechanism, which applies to the (110) and (102) surfaces, and partially so for the (114) surface, involves slight relaxation of sub-surface metal atoms towards the bulk region. This is technically not a reconstruction mechanism as bonds are neither broken nor formed.

The adsorption of species on the CuFeS_2 surface has also been investigated. De Lima *et al.* studied the adsorption of water at reconstructed (001) surfaces using DFT with the PBE functional [86]. For the S-terminated surface, it was concluded that the

most stable adsorption centre is Fe, followed by Cu. The stability of the Fe adsorption centre was attributed to the larger amount of unoccupied Fe states, as opposed to Cu and S states, close to the Fermi level in the DOS. Dissociative adsorption was also found to be an exothermic process on this surface. For the (originally) metal-terminated surface, it was found that surface S₂²⁻ species sterically hindered the adsorption of water on Fe sites despite the availability of Fe electronic states. Instead, the water molecule was observed to form hydrogen bonds with S. In addition, it was found that due to the inability for water to adsorb on metal sites, adsorption was stronger on the S-terminated surface compared to the metal-terminated surface. De Lima *et al.* pointed out that the unfavourable adsorption at the metal-terminated surface suggests some hydrophobic character at that surface that could be related to the low reactivity of chalcopyrite surfaces.

In a later study, de Lima *et al.* studied the adsorption of hydrochloric and sulphuric acid at the S-terminated (001) surface, also using DFT-PBE [87]. It was found that both chloride (Cl⁻), bisulphate (HSO₄⁻) and sulphate (SO₄²⁻) species preferentially adsorb to surface iron sites while the most favourable adsorption site for protons (H⁺) were neighbouring S₂²⁻ sites. Interestingly, it was also observed that the S-S bond of the S₂²⁻ site lengthened significantly upon adsorption. The weakening of the S-S bond suggests that the effect of pH and chemical speciation on the surface plays an important role in the leaching process.

2.3.3 Cu(In,Ga)(S,Se)₂ surfaces

The general Cu(In,Ga)(S,Se)₂ (CIGS) family of chalcopyrite compounds have been the subject of extensive research in the last few decades due to their potential applications in semiconductor devices such as photodetectors, visible-light emitters and non-linear optical devices [88–93]. More recently, it was discovered that the electrical, optical and chemical properties of CIGS make them suitable materials, both functionally and economically, for thin film solar cells [46, 94]. As the conversion efficiency of the solar cell depends on the crystal orientation of the film [95, 96], one of the key recent research theme in this field is the elucidation of fundamental properties, including atomic and electronic structures and the thermodynamic stability, of surfaces. This allows the surface morphology to be determined thereby aiding the development of techniques to grow thin films with the optimal surface orientation.

The CIGS compounds are highly related to CuFeS₂ in that they adopt the same crystal structure (“isostructural”) and are also composed of either elements common

to both (Cu, S), or of elements from the same groups (I, III and VI) of the periodic table. Given the lack of fundamental studies on the atomic and electronic structure of CuFeS₂ surfaces, a review of recent studies of CIGS surfaces is useful as it is likely that some of the conclusions drawn from these studies are relevant to the CuFeS₂ system.

CuInSe₂ thin films have been grown on substrates such as glass, alumina and GaAs for studies since the 1970s when the material was identified as a possible candidate for photovoltaic devices [97–99]. Some of the early experimental studies of CuInSe₂ indicated that the cleavage planes in CuInSe₂ are probably {101}, {110} and {112} [100, 101].

Kahn *et al.* published the first investigation of the atomic structure of the (112) and ($\bar{1}\bar{1}\bar{2}$) surfaces of CuInSe₂, which were prepared by Ar⁺ sputtering followed by annealing and probed by low energy electron diffraction (LEED) [102]. It was concluded that the atomic structure at the surface exhibited a symmetry that was incompatible with the bulk order of the metal sublattice that was possibly due to randomisation of metal ions due to finite temperature effects or ion impact.

Shukri and Champness conducted the first comprehensive study of all the prominent planes in CuInSe₂ [103]. Shukri and Champness measured angles between adjacent cleaved surfaces with verification from X-ray Laue diffractometry on Bridgman-grown samples and confirmed that the main cleavage planes in CuInSe₂ are {112} and {101}. Cleavage planes in the {110} orientation were also found, albeit at a lower frequency. In addition, the {112}, {101} and {110} planes were concluded to be the *only* cleavage planes in the crystals. Microscopic examination of {110} planes revealed that such surfaces consisted of ridges with microfacets of the {112} orientation implying thermodynamic stability of {112} planes with respect to {110} planes.

More recent studies, both theoretical and experimental, of CuInSe₂ and other CIGS compounds, have confirmed the observations made by Shukri and Champness. Hunger *et al.* observed faceting of CuInS₂ (110) and (001) surfaces grown by molecular beam epitaxy (MBE) into (112) and ($\bar{1}\bar{1}\bar{2}$) facets [104]. *Complete* faceting was observed for the (110) surface, while only partial faceting was observed for the (001) surface. In addition, it was also observed for the latter that faceting was suppressed under Cu-rich growth conditions. They therefore concluded that {112} is the preferred growth plane for CuInS₂. Liao and Rockett used a hybrid sputtering and evaporation process to grow epitaxial Cu(In,Ga)Se₂ films with a (110)/(102) orientation [105]. The resulting surfaces were observed to consist entirely of (112) and ($\bar{1}\bar{1}\bar{2}$) facets. It was therefore concluded that the polar (112) and ($\bar{1}\bar{1}\bar{2}$) surfaces have much lower surface energies than the nonpolar (110) and (102) surfaces. Siebentritt *et al.* used electron microscopy

to study {001} surfaces of CuGaSe₂ and CuInSe₂ grown by metal organic vapor phase epitaxy (MOVPE) [106]. It was observed that both surface show increasing faceting into (112) and $(\bar{1}\bar{1}\bar{2})$ facets with decreasing Cu content implying that the surface morphology and hence the surface energies depended on the growth conditions.

On the theoretical side Jaffe and Zunger performed DFT-LDA calculations on the (110) surface and (112)/ $(\bar{1}\bar{1}\bar{2})$ surface pair of CuInSe₂ [107]. The defect-free (112) and $(\bar{1}\bar{1}\bar{2})$ surfaces were found to have a higher surface energy than the (110) surface. However, under Cu-poor conditions the 1x1-(112) surface was predicted to be stabilised by a Cu vacancy pair in Cu-poor conditions, and by a Cu-on-In antisite in In-poor conditions while the 1x1- $(\bar{1}\bar{1}\bar{2})$ surface was predicted to be stabilised by a subsurface In-on-Cu antisite. In all cases, the defects stabilise the surface such that it is thermodynamically preferred over the (110) surface. Zhang and Wei also performed DFT-LDA calculations on the (110) surface and (112)/ $(\bar{1}\bar{1}\bar{2})$ surface pair of CuInSe₂ and reached the same conclusions as Jaffe and Zunger [108]. Moreover, they predicted that the 1x1-(112) surface with a (Cu,In) vacancy pair had a surface energy lower than the (110) surface. The theoretical studies provided confirmation of the experimental observations regarding the stability of the (112) and $(\bar{1}\bar{1}\bar{2})$ CIGS surfaces in addition to the dependence of the surface morphology on the growth conditions.

The stability of the (112) and $(\bar{1}\bar{1}\bar{2})$ surfaces relative to the (110) surface observed in CIGS compounds are surprising because of two reasons. First, for binary zinc-blende compounds such as ZnO which adopt the same crystallographic structure as CuFeS₂, (110) is usually the most stable surface and is hence the natural cleavage plane [109–111]. Second, the (112) and $(\bar{1}\bar{1}\bar{2})$ are polar surfaces in contrast to the (110) surface which is nonpolar. According to Tasker, nonpolar surfaces are likely to be much more stable with respect to polar surfaces due to high energy associated with the reconstruction of the surface required to quench the dipole moment perpendicular to the surface [112]. It should be noted that while Tasker’s classifications can serve as a useful way to predict the stability of surfaces, it is the presence of surface excess charge that points to the instability of a surface. This is discussed further in Section 3.4.1.

It is likely that several factors contribute to the surprising stability of the (112) and $(\bar{1}\bar{1}\bar{2})$ facets in CIGS compounds. First, is the fact that the slab can be considered as only slight polar. As seen in Figure 2.3, the anionic and cationic atomic layers within each repeating unit in the isostructural CuFeS₂ slab bounded by the metal-terminated (112) surface and the S-terminated $(\bar{1}\bar{1}\bar{2})$ surface are only slightly separated in the direction perpendicular to the surface. Consequently, the electrostatic dipole perpendicular to the surface is small, which suggests that the reconstruction required

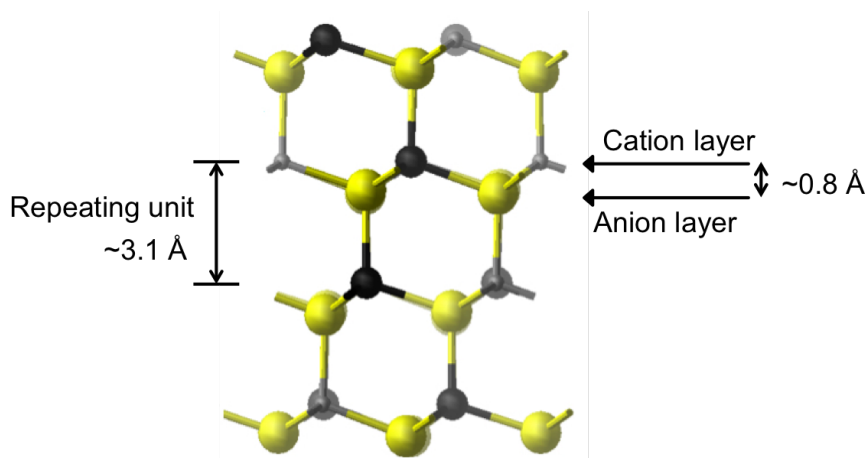


Figure 2.3: Structure of the CuFeS_2 slab bound by the (112) (top) and $(\bar{1}\bar{1}\bar{2})$ (bottom) surfaces based on the B3LYP optimised geometry of the bulk. Copper, iron and sulphur atoms are coloured black, silver and yellow respectively.

to stabilise the surface may be limited.

Second, is the consideration of bonding type and surface bond density, as discussed by Shukri and Champness [103]. For compounds such as silicon and germanium, which like CIGS compounds adopt the tetrahedral diamond structure, the covalent nature of their bonding means there is no Coulombic attraction between atomic layers. Consequently, the stability of the surface in these compounds is mainly governed by the density of bonds broken upon formation of the surface. The $\{111\}$ surfaces, analogous to the $\{112\}$ surfaces in $\text{A}^{\text{I}}\text{B}^{\text{III}}\text{X}_2^{\text{VI}}$ compounds, have the lowest surface bond density out of all surfaces and hence are observed to be the main cleavage planes in these compounds. On the contrary, binary zinc blende compounds have significant ionic character and the composition of atomic layers varies between different surfaces. The atomic layers of (110) surfaces are stoichiometric and hence charge neutral, while those of $\{111\}$ surfaces consist of exclusively cations or anions. Consequently, the Coulombic attraction between atomic layers is weaker for (110) compared to $\{111\}$. These inferences were used to explain why in such compounds the main cleavage plane is (110) and not $\{111\}$ despite the higher density of surface bonds in the former. Shukri and Champness suggested that CuInSe_2 could be less ionic than zinc blende compounds to an extent that the Coulombic attraction between atomic planes plays less of a role compared to the surface bond density in determining its cleavage properties. This explains their observations that cleavage along $\{112\}$ occurs more readily and also the observation of $\{112\}$ microcleavages on the (110) surface.

Third, is a stabilisation mechanism due to defects. While the formation of point defects are energetically costly in general, DFT-LDA calculations performed by Jaffe and Zunger, and Zhang and Wei both showed that with the right combination of surface defects and growth conditions, the (112) and ($\overline{112}$) surfaces of CuInSe_2 are thermodynamically preferred over the (110) surface [107, 108]. This is supported by previous DFT-LDA calculations, by Zhang *et al.*, which show the formation energy of certain defects in the bulk, such as the defect pair $2V_{\text{Cu}}^- + \text{In}_{\text{Cu}}^+$, is unusually low [113]. It was suggested that the low defect energy is related to the availability of two heterovalent cationic species in a (partially) ionic system that allows large inter-defect electrostatic interactions. The involvement of a defect-induced stabilisation mechanism to suppress the electrostatic dipole also explains observations made in several experimental studies that the growth conditions has an affect on the surface morphology in CIGS compounds [104–106, 114].

2.4 Summary

In this chapter, an overview of the literature relevant to this project has been given. Despite a significant body of research dedicated to experimental leaching studies, the complex interplay between the numerous species present in the system with the leaching conditions means there is no clear consensus of dissolution mechanisms. This is evident in the large number of proposed dissolution models. Regardless, it is clear that Cu dissolution of CuFeS_2 is a redox process that involves oxidation of Cu^+ in CuFeS_2 into Cu^{2+} into solution coupled with the reduction of an oxidising agent, as seen in the overall reaction of all proposed dissolution mechanisms.

On the contrary, the properties of bulk CuFeS_2 in the gas phase are generally well established. The geometric structure of CuFeS_2 is well documented to be that of a doubled zinc-spheralite cell, with ordered arrangement of Cu and Fe species within the cationic sublattice. Theoretical structural parameters obtained from DFT calculations with appropriate approximations to exchange-correlation have accurately reproduced the experimental counterparts. Although it has been known for a long time that CuFeS_2 is semiconducting, there is still considerable uncertainty in the value of the band gap with values ranging from 0.53 to 2.6 eV predicted by experimental and 0.0 to 1.82 eV by theoretical studies. It should be noted that the hybrid-exchange B3LYP functional, which is known to reliably reproduce the band gap in a range of semi-ionic and ionic semiconductors, predicts a band gap value of 1.82 eV. The antiferromagnetic ground state of CuFeS_2 , which consists of aligned Fe spins within the crystallographic *a-b*

plane and alternating spins along the crystallographic c direction, is well known. The oxidation state of CuFeS_2 has been subject to widespread debate, primarily due to the lower than expected magnetic moment of Fe in CuFeS_2 relative to that of isolated Fe^{3+} . However, recent studies employing several spectroscopic techniques generally support the $\text{Cu}^+\text{Fe}^{3+}(\text{S}^{2-})_2$ state, while providing evidence that the low Fe magnetic moment is due to strong covalent interactions between Fe and S.

The surface composition of CuFeS_2 has been studied extensively, usually as part of experimental leaching studies. However, relatively little is known about the properties of pure CuFeS_2 surfaces as limited research has been carried out to elucidate fundamental properties of CuFeS_2 surfaces. The geometry and electronic structure of a few selected surfaces have been investigated using DFT, leading to the identification of three distinct surface reconstruction mechanisms. The adsorption of small molecules on the (001) CuFeS_2 surface has also been studied to deduce potential ramifications for the surface reactivity. However, as surface energetics was not a focus of these studies, the surface morphology of CuFeS_2 remains unknown. This is not the case for CIGS compounds, analogous to CuFeS_2 in terms of structure and valency, as their surface properties, including energetics and morphology, have been more thoroughly investigated due to their application in thin-film solar cells. Notably, it has been observed both experimentally and theoretically, that the polar (112) and $(\bar{1}\bar{1}\bar{2})$ surfaces are thermodynamically stable with respect to the non-polar (110) surface. This is in spite of the fact that the non-polar surfaces are typically lower in energy than polar surfaces as reconstruction of the latter to quench the electrostatic dipole may be energetically costly. DFT calculations show that for CuInSe_2 , the stability of the (112) and $(\bar{1}\bar{1}\bar{2})$ surfaces are attributed to the low formation energy of defects due to the availability of two cation species different in oxidation state. The interesting properties of CIGS surfaces are relevant to this work, as it is possible that the trends observed in the CIGS surfaces, also apply to CuFeS_2 .

3

Theoretical Methods

This chapter will first discuss the total energy methods that are relevant to this work. The methods discussed are classical molecular mechanics (Section 3.1), quantum mechanical electronic structure methods (Section 3.2) as well as hybrid quantum mechanics/molecular mechanics (Section 3.3). In Section 3.4 and 3.5, various theoretical concepts relevant to the modelling of surfaces are outlined. In particular, the finite embedded cluster method, which is utilised in Chapter 6, is introduced. Finally, various algorithms used for geometry optimisation are described in Section 3.6.

3.1 Molecular mechanics

In the early 20th century, it became apparent from experimental spectroscopic data that the force constants and equilibrium bond lengths of similar bond types (e.g. C-C single bonds) were largely consistent for a wide range of molecules. The realisation of the transferable nature of bond parameters stimulated the development of classical molecular mechanics (MM), which uses parameterised functional forms to predict the energy of systems purely based on its conformation. Even with recent development of more accurate methods based on quantum mechanics (QM) (see Section 3.2), MM is still commonly used today. This is because many problems in computational chemistry and material science cannot be tackled using QM methods due to the unfavourable scaling of computational costs with system size. As MM is based on classical mechanics, the electronic degrees of freedom are neglected, which means the total energy is a function purely of the nuclear positions. Despite significant simplifications, MM calculations on systems that the employed model have been parameterised for can often deliver results as accurate as those derived from QM calculations at a tiny fraction of the

computational cost.

In an MM model, also referred to a force field, the total energy is a sum of various terms, each of which represent a different type of interaction that can distort the system. The interaction types can involve bonded or non-bonded atoms and are normally represented using simple, parametrised functional forms derived from experiment or from higher level calculations. Common bonded terms are bond stretching, valence angle bending and torsion, while common non-bonded terms describe van der Waals interactions and electrostatic interactions. Description of these terms are given in the following section.

3.1.1 MM terms

The material presented in this section is a brief summary of that found in References [1, 115, 116]. The reader is advised to consult these references for more in-depth discussion.

Bond stretching

Consider a bond between atoms A and B. The variation of the potential energy associated with the bond, U , as a function of the bond length, r_{AB} , is typically well described using the Morse potential whose functional form is shown in Eq 3.1 and typical shape is plotted in Fig 3.1.

$$U_{\text{Morse}}(r_{AB}) = D_{AB}[1 - \exp(-\alpha_{AB}(r_{AB} - r_0))]^2, \quad (3.1)$$

where the three derived parameters are D_{AB} , the bond dissociation energy, α_{AB} , a fitted parameter and r_0 , the equilibrium bond length.

As bond lengths do not usually distort significantly away from the natural bond length, it is often sufficient to model the bond stretching using a polynomial Taylor expansion about the equilibrium bond length truncated at the second order. This is equivalent to using Hooke's law, and the associated functional form is:

$$E_{\text{str}}(r_{AB}) = E_0 + \frac{k_{AB}}{2}(r_{AB} - r_0)^2, \quad (3.2)$$

where k_{AB} is the parametrised "force constant" for the A-B bond while E_0 is the zero point for the energy scale and is normally set to zero. A different k is typically parametrised for each bond type, which is specific to the identity of the bonded atoms and at times also the atomic environment surrounding the bond. The harmonic potential, which only requires 2 parameters, can accurately reproduce the Morse potential

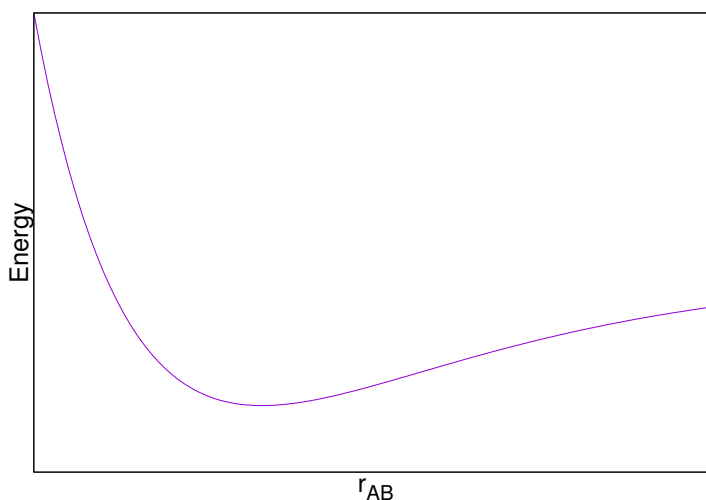


Figure 3.1: The functional form of the Morse potential (Equation 3.1 as a function of the bond length r_{AB}).

for bond lengths close to the natural bond length.

One limitation of the harmonic potential is the inability to reproduce the anharmonicity of the Morse potential. In addition, bonds that distort significantly away from the natural bond length can result in inaccurate results. If required, the harmonic potential can be improved by including additional terms of the Taylor expansion, albeit with a higher associated computational cost and additional complication in parametrisation. For example bond stretching terms of the MM2 potential includes cubic terms while quartic terms are also included for the MM3 potential. For systems where extreme bond distortion is expected, it may be desirable to use the Morse potential to reproduce the limiting behaviour.

As an illustration, a comparison of the parametrised Morse, harmonic and quartic functional forms with the exact stretch potential of the C-H bond in CH_4 about the equilibrium bond length is given in Figure 3.2. The figure illustrates how well the Morse potential reproduces the exact potential. It also shows that the harmonic potential closely matches the exact potential at bond lengths very close to the equilibrium ($\delta r < 0.1 \text{ \AA}$) but has an increasing error away from equilibrium. With the addition of cubic and quartic terms, the potential is almost inseparable from the Morse potential.

The Morse potential and the harmonic potential are pair potentials commonly used in molecular systems. However, these potentials may be inadequate for solid systems where many body effects can play an important role. In such systems, multibody

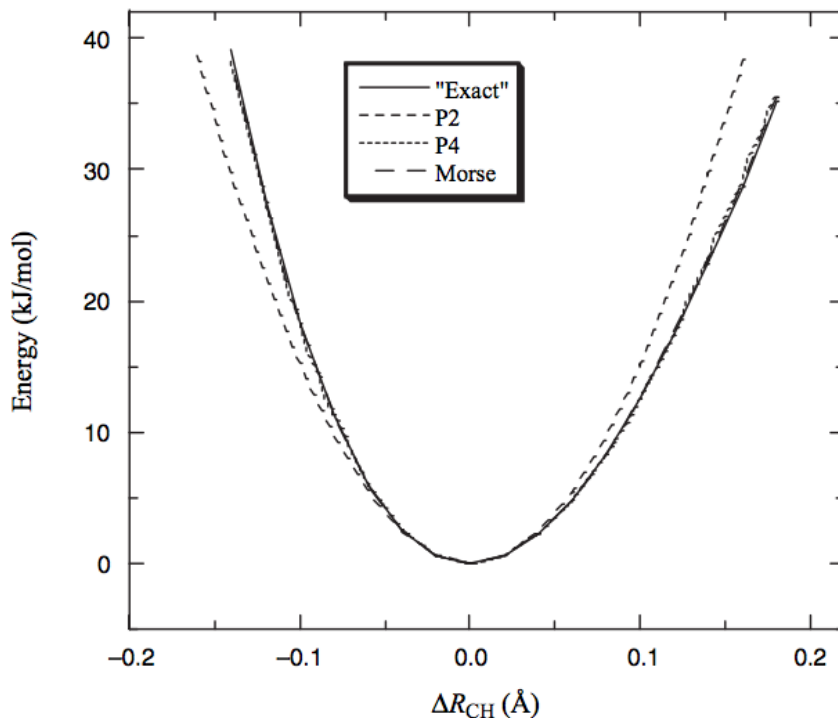


Figure 3.2: Comparison of the parametrised Morse, harmonic and quartic polynomial stretch potentials with the exact stretch potential of the C-H bond in CH_4 . Reproduction of Figure 2.3 in Reference [1] (Permission to reproduce is shown in Appendix B).

potentials such as the embedded atom model potential can be used.

Valence angle bending

Consider 3 bonded atoms, A-B-C, as shown in Figure 3.3. In MM, the valence angle is defined as the angle between bonds A-B and B-C. It has been shown from vibrational spectroscopy that energy change due to small variations of the valence angle about equilibrium are well approximated by polynomial Taylor expansions about the equilibrium bond angle θ_0 . As with bond stretching terms, the Taylor expansion is normally truncated at the second order, giving the harmonic potential:

$$E_{\text{valence}}(\theta_{\text{ABC}}) = \frac{k_{\text{ABC}}}{2}(\theta - \theta_0)^2, \quad (3.3)$$

where k_{ABC} is the parametrised force constant that characterises the stiffness of the A-B-C bond angle. The use of the harmonic potential is, like for bond stretching, a

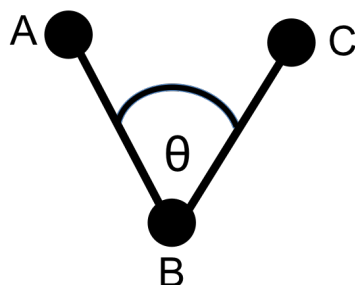


Figure 3.3: The valence (A-B-C) angle between 3 connected atoms.

compromise between simplicity (both computational and parametrisation) and accuracy. Higher order terms can be included to improve accuracy or to treat pathological cases such as highly strained molecules. The MM2 force field for example includes a quartic term [117].

Torsion

The torsional angle associated with 4 consecutively connected atoms A-B-C-D is defined as the angle between the two outer bonds (A-D and C-D) when they are projected onto the plane bisecting the central bond, as shown in Figure 3.4. Torsion energy terms are included to reproduce the variation in energy due to rotation of a structure about bonds. In addition, the torsion energy is used to correct inaccuracies in the other bonded terms. This term is a function of the torsional angle of 4 atoms bonded in sequence. By construction, the torsion angle is periodic with a period of 2π . The torsion energy term is therefore conventionally represented as a Fourier series, in other words a sum of sinusoidal functions:

$$E_{\text{torsion}}(\omega_{\text{ABCD}}) = \frac{1}{2} \sum_{\{j\}} V_{j,\text{ABCD}} [1 + (-1)^{j+1} \cos(j\omega_{\text{ABCD}} + \psi_{j,\text{ABCD}})], \quad (3.4)$$

where ω_{ABCD} is the torsional angle, $\{j\}$ is a set of integers that specify periodicities and V_j is the amplitude associated with the j -th periodicity. The $j = 1$ term has a period of 360° , the $j = 2$ term has a period of 180° and in general the $j = n$ term has a period of $360^\circ/n$. The set of $\{j\}$ included in the sum and the associated V_j values are specific to the torsional linkage A-B-C-D. In general the first three terms ($j = 1, 2, 3$) are included as this is often sufficient to qualitatively reproduce most rotational energy profiles. For each unique connected set of four atoms A-B-C-D, three torsional parameters,

V_1 , V_2 and V_3 therefore need to be determined. Not all force fields include torsional terms as sometimes non-bonded terms are sufficient to accurately reproduce equilibrium structures.

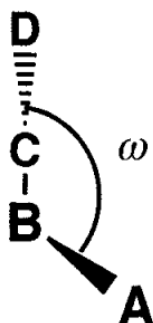


Figure 3.4: Illustration of the torsional angle between 4 connected atoms.

Improper torsional terms, or out-of-plane bending terms, involve 4 atoms that are not consecutively connected to each other. An example is acetone, shown in Figure 3.5, in which the central carbon atom is bonded to 3 other atoms.

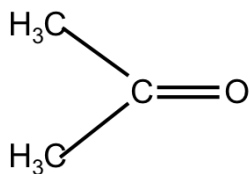


Figure 3.5: The structure of acetone.

Improper torsional terms are used for systems where bond stretching, valence angle and torsional terms are not sufficient to reproduce the desired geometry. For example, improper torsional terms are used to force co-planarity of the oxygen atom with the butane ring in cyclobutanone [115].

Electrostatic energy

In general, the distribution of electron charge in a system is not uniform due to differences in electronegativity. In most MM models, the associated electrostatic interaction energy is simply modelled assuming classical Coulombic interaction between point charges located at the atomic positions. The magnitudes of the point charges are normally parametrised to reproduce the electrostatic potential of the system calculated

using QM methods. Alternatively, empirical rules (e.g. Ref [118]) can be used to assign the point charges. The total Coulombic energy term is then simply the sum of the classical Coulombic energy between all pairs of atomic charges Q_A and Q_B within the system:

$$E_{\text{Coulomb}} = \sum_{A,B} \frac{Q_A Q_B}{\epsilon r_{AB}}, \quad (3.5)$$

where ϵ is an “effective” dielectric constant which accounts for polarisation effects due to the environment of the system. For example, a ϵ value of 1 is normally used in vacuum, while a higher value would be used in a solvent to reduce the effect of long-range interactions. For atoms separated by up to a few bonds, electrostatic terms are usually neglected or scaled down by a factor, as the bonded terms are parameterised to include all interactions. As the number of atom pairs in the system scales quadratically with the number of atoms, a significantly large number of interactions need to be considered for a large system.

An alternative approach to calculate the electrostatic interaction energy in molecular systems is via the central multipole expansion in which each molecule is considered as a single entity. In this multipole approach, the charge distribution associated with a molecule is represented as an infinite sum of the monopole, dipole, quadrupole, octopole and so on. The electrostatic interaction energy is then the sum of the electrostatic energies of molecule pairs modelled by their lowest non-zero dipole moment. For charged species such as Cu^{2+} and SO_4^{2-} this is their charge while for neutral molecules it is a higher electric moment such as the dipole (e.g. H_2O) or quadrupole (e.g. N_2).

In the above, only interactions of static electrostatic moments have been considered. This may be insufficient for systems which are highly polarisable, in other words for systems which have easily perturbed electric moments under an electric field. In such cases, the force field can be extended by assigning a polarisability tensor to each atom and following an iterative procedure to determine the induced dipole moments.

An alternative, simpler, method to model polarisation is the shell model of Dick and Overhauser, illustrated in Figure 3.6, in which each atom is separated into two components: a positive nucleus and a negative shell, which represents the surrounding electron cloud [119]. The nucleus and shell are coupled via a spring with an associated spring constant. For each atom type three parameters need to be derived: the charges of the nucleus and shell, and the spring constant. Moreover, neighbouring shells may themselves be coupled which would require additional spring constant parameters to be derived. Dielectric properties can be used to determine the parameters.

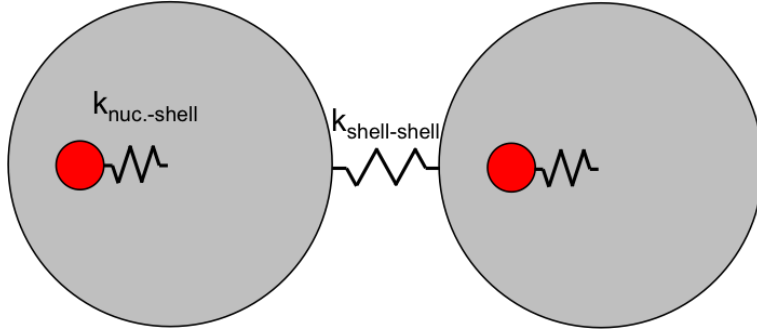


Figure 3.6: Illustration of the shell model of Dick and Overhauser. The figure shows two polarised atoms. The positive nuclei are the small red circles while the negative shells are the large grey circles.

Van der Waals energy

The van der Waals energy term models all non-bonded interactions excluding electrostatic interactions, and comprises a combination of repulsive and attractive contributions.

The attractive contribution is due to London dispersive interactions, which is a quantum mechanical effect that arises because of fluctuations in the electron clouds leading to instantaneous dipoles which in turn induce dipoles in neighbouring atoms. The result is an attractive force between instantaneous and induced dipoles. The Drude model can be used to estimate the dispersion energy by modelling the fluctuations in the electron clouds using the multipole expansion, which is sum of an oscillating dipole, quadrupole, and so on. By solving the appropriate Schrödinger equations, the dispersive interaction energy between two molecules is given as the following series expansion:

$$E_{\text{drude}}(\mathbf{r}) = \frac{C_6}{r^6} + \frac{C_8}{r^8} + \frac{C_{10}}{r^{10}} + \dots, \quad (3.6)$$

where all the coefficients C_n are negative, implying that the interaction is attractive.

The repulsive contribution is also a quantum mechanical effect that is a consequence of Pauli's exclusion principle, which prevents any two electrons in a system from having the same set of quantum numbers. As result, there is a reduction in the electron density in volumes between nuclei, which leads to electrostatic repulsion between incompletely shielded nuclei. This is a short range effect that is referred to as exchange interactions. The associated energy is inversely proportional ($\sim 1/r$) to the internuclear separation at very short internuclear separations and exhibits exponential decay ($\sim e^{-r}$) for larger separations.

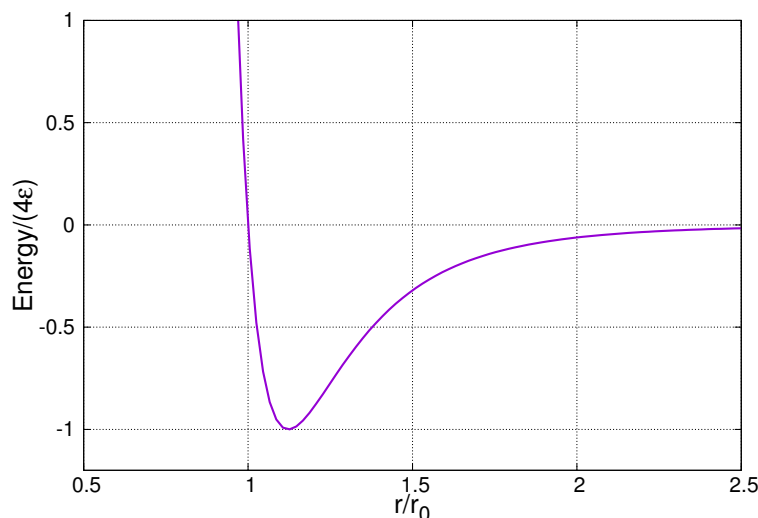


Figure 3.7: Plot of the Lennard-Jones 12-6 potential (Equation 3.7) with $\epsilon = \sigma = 1$.

The total van der Waals energy term combines the energy due to repulsive exchange interactions with the attractive dispersion interactions. As the total number of non-bonded terms scales quadratically with the number of atoms in the system, it is desirable, particularly for large systems, for a functional form that is readily computed.

One of the most commonly used van der Waals energy potentials is the Lennard-Jones (LJ) 12-6 potential:

$$E_{\text{LJ}12-6}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right], \quad (3.7)$$

where ϵ is the well depth and σ is the separation at which the energy is zero (also known as the ‘collision diameter’). The well-known shape of the LJ 12-6 potential is plotted in Figure 3.7. The second term of the potential is the leading term of the full Drude model series expansion. The neglect of higher order terms is justified as the C_6 term, which represents solely the dipole-dipole interactions, usually accounts for most of the dispersion energy. In addition, this approximation has the benefits of lower computational cost and simple parameterisation. The first term is the repulsive term its functional form has no strong theoretical basis, but has shown to be reasonable for systems such as rare gases. The exponent of 12 is deliberately chosen to be double that of the attractive part as it allows the repulsive term to be rapidly computed through squaring of the attractive r^{-6} term. The LJ 12-6 potential is also commonly expressed

in the following alternative, equivalent forms:

$$E_{\text{LJ } 12-6}(r) = \epsilon \left[\left(\frac{r_m}{r} \right)^{12} - 2 \left(\frac{r_m}{r} \right)^6 \right], \quad (3.8)$$

or

$$E_{\text{LJ } 12-6}(r) = \frac{A}{r^{12}} - \frac{C}{r^6}. \quad (3.9)$$

In Eq. 3.8, r_m is the separation at which the first derivative of the energy is zero and hence the energy function is at a minimum.

The LJ parameters are specific for each pair of atoms. This implies that for a system of N species of atoms, $N(N-1)/2$ sets of parameters need to be derived, which can be difficult and time consuming. It is therefore common to derive only parameters for pure atom interactions (i.e. atom interacting with its own type) and obtain parameters for cross interactions using *mixing rules*. One of the most commonly used for LJ interactions is the Lorentz-Bethelot mixing rules, in which the collision diameter σ_{AB} for the A-B mixed interaction is given by:

$$\sigma_{AB} = \frac{1}{2}(\sigma_{AA} + \sigma_{BB}), \quad (3.10)$$

and the corresponding well depth ϵ_{AB} is given by:

$$\epsilon_{AB} = \sqrt{\epsilon_{AA}\epsilon_{BB}}. \quad (3.11)$$

For other systems such as hydrocarbons where the repulsive term in the LJ 12-6 function is too steep, lower exponents (such as 9, or 10) are often used for the repulsive term. One of the main alternatives to the LJ potential is the Buckingham potential, in which the repulsive term has an exponential functional:

$$E = Ae^{-r/\rho} - C/r^6. \quad (3.12)$$

Some force fields use the Buckingham potential to more accurately reproduce the exchange energy.

3.1.2 Advantages and disadvantages of molecular mechanics

The avoidance of calculating the electronic wavefunction and the use of simple functional forms for various interactions means that in general, MM methods are computationally efficient thereby allowing simulations of large systems (100,000+ atoms) over

long timescales (nanoseconds or more). With careful parametrisation, a force field can accurately reproduce some structural properties such as specific ground state structures and elastic constants. However, due to significant underlying approximations, such as the implicit assumption that the potential describing bonding is separable into different (bond, angle and torsion) terms, no force field is able to comprehensively model *all* structural properties pertinent to a system. Furthermore, most MM models cannot simulate breaking and forming of bonds due to the functional forms of the bonding terms, which means they are incapable of studying chemical reactions. Reactive force fields are an exception as they are designed to enable the modelling of bond formation and breakage. An example of a reactive force field is the ReaxFF (“reactive force field”) potential which utilises the “bond order”, a measure of the bond type and strength, as a parameter in the interactions terms [120].

3.2 Electronic structure methods

One of the key limitations of MM methods is the inability to describe the electron distribution due to neglect of the electronic degrees of freedom. This has led to the development of electronic structure methods, in which the central theme is to solve the Schrödinger equation. In general, the time independent Schrödinger equation for a system with n electrons and N nucleons is:

$$\hat{H}\Psi = \left[\sum_{\alpha=1}^N \left(-\frac{\hbar^2}{2M} \nabla_{\mathbf{R}_\alpha}^2 \right) + \sum_{i=1}^n \left(-\frac{\hbar^2}{2m} \nabla_{\mathbf{r}_i}^2 \right) - \sum_{i=1}^n \sum_{\alpha=1}^N \frac{Z_\alpha e^2}{4\pi\epsilon_0 |\mathbf{r}_i - \mathbf{R}_\alpha|} - \frac{1}{2} \sum_{i=1}^n \sum_{j=1(\neq i)}^n \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_i - \mathbf{r}_j|} + \frac{1}{2} \sum_{\alpha=1}^N \sum_{\beta=1(\neq \alpha)}^N \frac{Z_\alpha Z_\beta e^2}{4\pi\epsilon_0 |\mathbf{R}_\alpha - \mathbf{R}_\beta|} \right] \Psi = E\Psi \quad (3.13)$$

The first term of the expanded Hamiltonian $\hat{H}$ is the kinetic energy of all nuclei (α). The second term is the kinetic energy of all electrons (i). The third, fourth and fifth terms are respectively the sum of the nuclear-electron, electron-electron and nuclear-nuclear potential energies. The wavefunction of the system, Ψ , is a function of the positions of all nuclei and electrons:

$$\Psi = \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n, \mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N) \quad (3.14)$$

By defining the following n -dimensional vectors:

$$\mathbf{r} = (\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n) \quad (3.15)$$

$$\nabla_{\mathbf{r}} = (\nabla_{\mathbf{r}_1}, \nabla_{\mathbf{r}_2}, \dots, \nabla_{\mathbf{r}_n}) \quad (3.16)$$

and the following N -dimensional vectors:

$$\mathbf{R} = (\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N) \quad (3.17)$$

$$\nabla_{\mathbf{R}} = (\nabla_{\mathbf{R}_1}, \nabla_{\mathbf{R}_2}, \dots, \nabla_{\mathbf{R}_N}) \quad (3.18)$$

the Schrödinger equation defined in Eq. 3.13 can be rewritten more simply as:

$$\left[\frac{\hbar^2}{2M} \nabla_{\mathbf{R}}^2 - \frac{\hbar^2}{2m} \nabla_{\mathbf{r}}^2 + V(\mathbf{r}, \mathbf{R}) \right] \psi(\mathbf{r}, \mathbf{R}) = E\psi(\mathbf{r}, \mathbf{R}), \quad (3.19)$$

where the potential energy $V(\mathbf{r}, \mathbf{R})$ is:

$$V(\mathbf{r}, \mathbf{R}) = - \sum_i \sum_{\alpha} \frac{Z_{\alpha} e^2}{4\pi\epsilon_0 |\mathbf{r}_i - \mathbf{R}_{\alpha}|} + \frac{1}{2} \sum_i \sum_{j(\neq i)} \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_i - \mathbf{r}_j|} + \frac{1}{2} \sum_{\alpha} \sum_{\beta(\neq \alpha)} \frac{Z_{\alpha} Z_{\beta} e^2}{4\pi\epsilon_0 |\mathbf{R}_{\alpha} - \mathbf{R}_{\beta}|}. \quad (3.20)$$

By using the Hartree atomic units listed in Table 3.1, the Schrödinger equation can be further simplified into the following dimensionless form:

$$\left[\frac{1}{2M} \nabla_{\mathbf{R}}^2 - \frac{1}{2} \nabla_{\mathbf{r}}^2 + V(\mathbf{r}, \mathbf{R}) \right] \psi(\mathbf{r}, \mathbf{R}) = E\psi(\mathbf{r}, \mathbf{R}), \quad (3.21)$$

where M is now the nuclear mass (in atomic units), and $V(\mathbf{r}, \mathbf{R})$ is now:

$$V(\mathbf{r}, \mathbf{R}) = - \sum_i \sum_{\alpha} \frac{Z_{\alpha}}{|\mathbf{r}_i - \mathbf{R}_{\alpha}|} + \frac{1}{2} \sum_i \sum_{j(\neq i)} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \frac{1}{2} \sum_{\alpha} \sum_{\beta(\neq \alpha)} \frac{Z_{\alpha} Z_{\beta}}{|\mathbf{R}_{\alpha} - \mathbf{R}_{\beta}|}. \quad (3.22)$$

Type	Value in SI units	Description
Mass	9.109382×10^{-31} kg	Electron rest mass (m_e)
Charge	1.602176×10^{-19} C	Elementary charge (e)
Action	1.054572×10^{-34} Js	Reduced Planck's constant ($\hbar$)
Electric Constant	8.987552×10^9 kgm ³ s ⁻² C ⁻²	Coulomb force constant [$1/(4\pi\epsilon_0)$]

Table 3.1: Description of the Hartree atomic units and their equivalent values in SI units.

Due to the Coulombic repulsion terms, the exact solution cannot be obtained with the exception of the most trivial of systems (such as the hydrogen atom). Approximations are therefore necessary to make the equation tractable. As in classical molecular mechanics, it is useful to consider the fact that electrons are much lighter than nuclei which means the nuclei are effectively stationary from the point of view of the electrons. The Born-Oppenheimer approximation, which separates the electronic and nuclear degree of freedom, can therefore be applied, resulting in isolation of the electronic Schrödinger equation:

$$\left[-\frac{1}{2}\nabla_{\mathbf{r}}^2 + V(\mathbf{r}, \mathbf{R}) \right] \phi_i(\mathbf{r}; \mathbf{R}) = E_i(\mathbf{R})\phi_i(\mathbf{r}; \mathbf{R}). \quad (3.23)$$

Here, $\phi_i(\mathbf{r}; \mathbf{R})$, are electronic eigenfunctions with associated eigenvalues, $E_i(\mathbf{R})$, for a fixed set of nuclear positions $\mathbf{R}$. The Born-Oppenheimer approximation is assumed from here on.

One of the fundamental concepts of quantum mechanics is that the expectation value of an observable associated with the operator $\hat{O}$ for any general normalised wave function Ψ is given by

$$\int \dots \int \Psi^* \hat{O} \Psi d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_n \equiv \langle \Psi | \hat{O} | \Psi \rangle, \quad (3.24)$$

where Ψ^* is the complex-conjugate of Ψ . The right hand side of the statement is equivalent to the left hand side but written more conveniently in Dirac notation. The general strategy for finding the ground state wave function and energy involves invoking the *variational principle* which states that the energy computed via the expectation value of the Hamiltonian operator from any trial wavefunction, E_{trial} , is an upper bound to the true ground state energy E_0 :

$$\langle \Psi_{\text{trial}} | \hat{H} | \Psi_{\text{trial}} \rangle = E_{\text{trial}} \geq E_0 = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle, \quad (3.25)$$

where equality only holds if Ψ_{trial} is identical to Ψ_0 .

Finding the ground state wave function and energy therefore involves searching through all valid wave functions and identifying the one that minimises the total energy. Without further approximations, this is still an impossibly difficult task except for the smallest of systems, because the complicated electron-electron interaction term is still present and also the wavefunction is expressed in a $3N$ -dimensional space.

3.2.1 The Hartree-Fock approximation

One of the mainstream electronic structure methods is the Hartree-Fock (HF) method, which was developed in the 1920s soon after the discovery of the Schrödinger equation. The HF method assumes that the wavefunction is an antisymmetric Slater determinant to satisfy Pauli's exclusion principle. The theoretical framework of HF is described as follows.

Consider individual one-electron wavefunctions as spin orbitals, $\chi_i(\mathbf{r})$, formed from the product of a spatial orbital, $\phi_i(\mathbf{r})$, with a spin function, σ_i , which can be either α ("spin-up") or β ("spin-down"). If the spin-orbitals are orthonormal, the following relation holds:

$$\int \chi_i \chi_j dx = \langle \chi_i | \chi_j \rangle = \delta_{ij} , \quad (3.26)$$

where $x = (\mathbf{r}, s)$ is the combined spatial and spin co-ordinates, so any "integration" over x includes both a sum over spin indices and a spatial integral: $(\int dx \equiv \sum_s \int d\mathbf{r})$. In addition, $|\chi(\mathbf{r})|^2 dx = |\phi(\mathbf{r})\sigma|$ represents the probability of finding an electron with spin σ within the volume element $d\mathbf{r}$.

The approximation central to the HF method is that the solution to the n -electron wave function is a Slater determinant constructed using n orthonormal spin-orbitals as shown in Eq. 3.27.

$$\Psi_{\text{SD}} = \frac{1}{\sqrt{n!}} \begin{vmatrix} \chi_1(\mathbf{r}_1) & \chi_2(\mathbf{r}_1) & \cdots & \chi_n(\mathbf{r}_1) \\ \chi_1(\mathbf{r}_2) & \chi_2(\mathbf{r}_2) & \cdots & \chi_n(\mathbf{r}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(\mathbf{r}_n) & \chi_2(\mathbf{r}_n) & \cdots & \chi_n(\mathbf{r}_n) \end{vmatrix} . \quad (3.27)$$

By construction, Slater determinants are antisymmetric and therefore satisfy Pauli's exclusion principle. The ground state is then obtained via application of the variational principle. In practice this involves varying the spin orbitals under the constraint that they remain orthonormal and in such a way to minimise the energy, which is the expectation value of the Hamiltonian operator:

$$E_{\text{HF}} = \langle \Phi_{\text{SD}} | \hat{H} | \Phi_{\text{SD}} \rangle . \quad (3.28)$$

It can be shown by expanding the determinant that this energy, called the HF energy,

is equivalent to:

$$E_{\text{HF}} = \langle \Phi_{\text{SD}} | \sum_i \hat{h} | \Phi_{\text{SD}} \rangle + \frac{1}{2} \langle \Phi_{\text{SD}} | \sum_i \sum_{j(\neq i)} v_{ij} | \Phi_{\text{SD}} \rangle, \quad (3.29)$$

where the first part:

$$\langle \Phi_{\text{SD}} | \sum_i \hat{h} | \Phi_{\text{SD}} \rangle = \int \chi_i^*(\mathbf{x}) \left(-\frac{1}{2} \nabla^2 - \sum_{\alpha} \frac{Z_{\alpha}}{|\mathbf{r} - \mathbf{r}_{\alpha}|} \right) \chi_i(\mathbf{x}) d\mathbf{x}, \quad (3.30)$$

is the sum of the single-electron energies under the assumption that the electrons are non-interacting. The second part,

$$\begin{aligned} \langle \Phi_{\text{SD}} | \sum_i \sum_j v_{ij} | \Phi_{\text{SD}} \rangle &= \frac{1}{2} \sum_i \sum_{j(\neq i)} \int |\chi_i(\mathbf{x})|^2 \frac{1}{|\mathbf{r} - \mathbf{r}'|} |\chi_j(\mathbf{x}')|^2 d\mathbf{x} d\mathbf{x}' - \\ &\quad \frac{1}{2} \sum_i \sum_{j(\neq i)} \int \chi_i^*(\mathbf{x}) \chi_j^*(\mathbf{x}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \chi_j(\mathbf{x}') \chi_i(\mathbf{x}) d\mathbf{x} d\mathbf{x}', \end{aligned} \quad (3.31)$$

consists of two terms. The first term is the Hartree energy, which is the total Coulomb energy representing the electrostatic repulsion between the charge densities associated with the occupied orbitals. The second term is the exchange energy and it is purely a quantum mechanical quantity that arises as a result of the antisymmetric nature of the wavefunction. It is straightforward to show that when two electrons with the same spin approach each other the wavefunction vanishes. This implies that antisymmetry keeps like-spin electrons apart - this is the origin of Pauli's exclusion principle. The physical interpretation of the exchange energy is the reduction in the electron-electron Coulomb repulsion due to this quantum mechanical effect.

It can be shown, that to obtain the best possible single Slater determinant, in other words the one that minimises the energy, requires solving the HF equations:

$$\left[-\frac{1}{2} \nabla^2 - \sum_{\alpha} \frac{Z_{\alpha}}{|\mathbf{r}_i - \mathbf{r}_{\alpha}|} + \sum_j (\hat{J}_j(\mathbf{r}) - \hat{K}_j(\mathbf{r})) \right] \chi_i = \lambda_i \psi_i(\mathbf{r}) \chi_i, \quad (3.32)$$

where the Coulomb operator, $\hat{J}$ is:

$$\hat{J}_j(\mathbf{r}_1) = \int |\chi_j(\mathbf{r}_2)|^2 \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_2, \quad (3.33)$$

and the exchange operator, $\hat{K}$, when operating on a spin orbital leads to the following:

$$\hat{K}_j \chi_i(\mathbf{r}_1) = \int \chi_j^*(\mathbf{r}_2) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \chi_i(\mathbf{r}_2) d\mathbf{r}_2 \chi_j(\mathbf{r}_1). \quad (3.34)$$

The Coulomb term represents the electrostatic potential an electron at $\mathbf{r}_1$ experiences due to the average charge distribution of another electron in spin orbital χ_j . The exchange operator has the effect of exchanging the variables in the two spin orbitals.

The HF equations are eigenvalue equations where the eigenvalues λ_i are Lagrange multipliers that enforce normalisation of the spin-orbitals. The eigenvalues physically represent the orbital energies. In practice, the HF equations are solved by starting with a initial guess of the orbitals and then iteratively solving the HF equations until convergence of the electron density and energy is reached.

As seen in the HF equations, the Coulombic interaction is only modelled in an average sense, this is known as the mean field approximation. This means that at the infinite basis limit, the difference between the HF energy and the exact energy is the electron correlation energy. As correlation only accounts for a small portion of the total energy, HF is generally able to give qualitatively correct results, but is often unable to accurately describe chemical phenomena. This has lead to the development of post HF methods, which systematically improves upon HF theory by going beyond the assumption that the solution is a single Slater determinant.

Post HF methods can be divided into two broad classifications: those based on many body perturbation theory and those based on the variational principle. The former includes the MP2 and MP4 methods formulated by Møller and Plesset [121]. The latter includes the configuration interaction (CI) [122] and coupled-cluster (CC) methods [123]. While post HF methods have proven to be highly accurate, the computational cost of such methods scales to the fourth or higher power of the number of basis states, and therefore can only been applied to small systems. The neglect of electron correlation in HF and the steep computational cost of post HF methods has meant that DFT is most commonly used in QM computational chemistry. The theory and implementation of DFT is described in Sections 3.2.2 to 3.2.5.

3.2.2 The electron density as the fundamental variable

In DFT, the Schrödinger equation is simplified by considering the electron density, which only has 3 degrees of freedom representing the 3 spatial variables, as the fundamental variable. Though this may seem like an oversimplification, it is justified as the Hamiltonian, $\hat{H}$, consists of only operators that act on one ($\hat{T}$ and $\hat{V}_{\text{nuc-elec}}$) or at

most two particles ($\hat{V}_{\text{elec-elec}}$) at a time, regardless of system size.

In 1927, Thomas and Fermi were the first to attempt using the electron density ρ instead of the wavefunction to understand atomic and molecular systems [124, 125]. The electronic kinetic energy in their model was based on the uniform electron gas, a fictitious model system of constant electron density, while the potential energy, which includes nuclear-electron and electron-electron interactions, was modelled classically. The expression for the energy of an atom in the Thomas-Fermi model is:

$$E_{TF}[\rho(\mathbf{r})] = \frac{3}{10}(3\pi^2)^{2/3} \int \rho^{5/3}(\mathbf{r}) d\mathbf{r} - Z \int \frac{\rho(\mathbf{r})}{r} + \frac{1}{2} \int \int \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2. \quad (3.35)$$

The Thomas-Fermi model is a very coarse approximation, especially as exchange and correlation effects are completely neglected. Nevertheless, it showed that the electron density of a system could be mapped to its energy without any additional information. As the energy depends on the electron density which is itself a function of the spatial coordinates, the energy is said to be a functional of the electron density. The ground state of a system is then obtained via the variational principle, which involves varying the electron density to minimise the total energy under the constraint that the integral of electron density over all space corresponds to the total number of electrons n :

$$\int \rho(\mathbf{r}) d\mathbf{r} = n. \quad (3.36)$$

While the Thomas-Fermi model gives an expression where each term of the total energy is a functional of electron density, it fails miserably in reproducing basic qualitative results; it has been shown that within the Thomas-Fermi model that chemical bonding cannot exist as no molecular system is more stable with respect to its fragments. The main problem with the Thomas-Fermi model lies in the kinetic energy functional, as it poorly models the relationship between electron density and the kinetic energy.

3.2.3 The Hohenburg-Kohn theorems

In 1964, Hohenburg and Kohn published a seminal paper proving two theorems that lead to the birth of DFT [126]. The first Hohenburg-Kohn theorem states:

‘The external potential V_{ext} is (to within a constant) a unique functional of $\rho(\mathbf{r})$; since, in turn V_{ext} fixes $\hat{H}$ we see that the full many particle ground state is a unique functional of $\rho(\mathbf{r})$ ’

The theorem implies that the individual components of the energy are also functionals of the ground state electron density:

$$E_0[\rho_0] = T[\rho_0] + E_{ee}[\rho_0] + E_{\text{ext}}[\rho_0], \quad (3.37)$$

where $T[\rho_0]$ is the electronic kinetic energy, E_{ee} is the electron-electron repulsion energy and E_{ext} is the energy arising from interaction of electrons with the external potential. For simplicity, the external potential is considered to be purely due to the nuclei. It is useful to separate this total energy expression into terms which are system dependent - those that only depend on the number, positions and types of nuclei - and terms that are system independent:

$$E_0[\rho_0] = \int \rho_0(\mathbf{r}) V_{\text{ext}} d\mathbf{r} + T[\rho_0] + E_{ee}[\rho_0] = \int \rho_0(\mathbf{r}) V_{\text{ext}} d\mathbf{r} + F_{\text{HK}}[\rho_0]. \quad (3.38)$$

The system independent terms are combined into a new quantity, F_{HK} , called the Hohenberg-Kohn functional. If the form of the Hohenberg-Kohn functional is known, the Schrödinger equation can be solved exactly. Moreover, since the functional is system independent, it would apply to all possible systems. Unfortunately, the explicit form of the Hohenberg-Kohn functional is unknown and the best that can be done is to extract parts of the functional that are already known. For example the classical Coulombic energy of an electron density is well known so the total electron-electron repulsion energy can be rewritten as a sum of classical and non-classical contributions:

$$E_{ee}[\rho] = J[\rho] + E_{\text{non-classical}}[\rho], \quad (3.39)$$

where the classical contribution is:

$$J[\rho] = \frac{1}{2} \int \int \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2. \quad (3.40)$$

The second Hohenberg-Kohn theorem, is very similar to the variational theorem. The theorem states that the Hohenberg-Kohn functional $F_{\text{HK}}[\rho]$, delivers the lowest energy if and only if the input density is the true ground state density, ρ_0 . The importance of this theorem is that it gives a formal prescription of how to obtain the ground state density.

Together, the two Hohenberg-Kohn theorems proved that there is a unique mapping between the ground state density ρ_0 and the ground state energy. In other words, they

provided a rigorous method of solving the many-body Schrödinger equation using the electron density as the fundamental quantity. While the Hohenberg-Kohn theorems were certainly ground-breaking, it only showed in principle that there was a way to exactly solve the Schrödinger equation to obtain the ground state. In reality, the functional forms are known for only some of the interactions. In fact, the Hohenberg-Kohn theorems do not even suggest how to approximate the unknown functionals.

The Kohn-Sham approach to DFT

Kohn and Sham published the second seminal paper of modern DFT in 1965 in which they prescribed a method of how to approximate the unknown functionals [127]. The Kohn-Sham approach provides a more accurate method of treating the kinetic energy by considering a non-interacting reference system, with the following Hamiltonian:

$$\hat{H}^S = -\frac{1}{2} \sum_i^n \nabla_i^2 + \sum_i^n V_S(\mathbf{r}_i) , \quad (3.41)$$

where V_S is an effective, local potential. It is known from HF theory that the ground state wavefunction of a non-interacting system is a Slater-determinant where the spin orbitals, called Kohn-Sham orbitals, are determined by solving the one-electron Kohn-Sham equations:

$$\hat{f}^{\text{KS}} \phi_i = \epsilon_i \phi_i , \quad (3.42)$$

where $\hat{f}^{\text{KS}}$, the one-electron Kohn-Sham operator is defined as

$$\hat{f}^{\text{KS}} = -\frac{1}{2} \nabla^2 + V_S(\mathbf{r}) . \quad (3.43)$$

To link this artificial non-interacting system with the real system, the effective potential V_S is chosen such that the sum of square moduli of the Kohn-Sham orbitals is equal to the ground state density of the real, interacting, target system:

$$\sum_i^n |\phi_i(x)|^2 = \rho_0(\mathbf{r}) . \quad (3.44)$$

The philosophy of the Kohn-Sham approach is to avoid determining the exact functional for each term of the total energy but instead concentrate on calculating as much possible in an exact manner while approximating the rest. Under this approach the kinetic energy is divided into a contribution from the non-interacting reference system,

which is known exactly, and an unknown residue part. The former is given by:

$$T_S = -\frac{1}{2} \sum_i^n \langle |\phi_i| \nabla^2 |\phi_i\rangle \quad (3.45)$$

The electron-electron interaction energy is divided into the known classical Coulombic energy and the non-classical contributions. The unknown terms are grouped together and form a term called the exchange-coorelation energy E_{XC} . The total energy in terms of the electron density is then:

$$E[\rho(\mathbf{r})] = T_S[\rho] + J[\rho] + E_{XC}[\rho] + E_{\text{ext}}[\rho] \quad (3.46)$$

Using equations 3.44 and 3.45, the total energy can be rewritten in terms of the Kohn-Sham orbitals:

$$E = -\frac{1}{2} \sum_i^N \langle \phi_i | \nabla^2 | \phi_i \rangle + \frac{1}{2} \sum_i \sum_j \int \int |\phi_i(\mathbf{r}_1)|^2 \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} |\phi_j(\mathbf{r}_2)|^2 d\mathbf{r}_1 d\mathbf{r}_2 + \\ E_{XC}[\rho(\mathbf{r})] - \sum_i^n \int \sum_\alpha^N \frac{Z_\alpha}{|\mathbf{r}_1 - \mathbf{r}_\alpha|} |\phi_i(\mathbf{r}_1)|^2 d\mathbf{r}_1. \quad (3.47)$$

Of course, since E_{XC} is unknown, it cannot be written in terms of the orbitals. By applying the variational principle, a set of equations, called the Kohn-Sham equations, representing the condition that the Kohn-Sham orbitals must meet in order to minimise the total energy can be obtained:

$$\left(-\frac{1}{2} \nabla^2 + \left[\int \frac{\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_2 + V_{XC}(\mathbf{r}_1) - \sum_\alpha^N \frac{Z_\alpha}{|\mathbf{r}_1 - \mathbf{r}_\alpha|} \right] \right) \phi_i = \epsilon_i \phi_i. \quad (3.48)$$

The Kohn-Sham equations are analagous to the HF equations in the HF approach. In order to fully incorporate the non-interacting reference, there needs to be a way of obtaining the Slater determinant characterised by the Kohn-Sham orbitals that combine to give the same electron density as the real system. By comparing equation 3.48 with equation 3.43, it is easy to see that the expression of the effective potential required to obtain the Kohn-Sham orbitals of the reference non-interacting system is:

$$V_S(\mathbf{r}) \equiv \int \frac{\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_2 + V_{XC}(\mathbf{r}_1) - \sum_\alpha^N \frac{Z_\alpha}{|\mathbf{r}_1 - \mathbf{r}_\alpha|}. \quad (3.49)$$

Note that V_{XC} , the exchange-correlation potential is defined as the functional derivative of E_{XC} with respect to ρ :

$$V_{\text{XC}} \equiv \frac{\delta E_{\text{XC}}}{\delta \rho}. \quad (3.50)$$

Since no approximations have been introduced yet, the exact ground state energy of the many-electron Schrödinger equation could be obtained if the functional forms of E_{XC} and V_{XC} were known. This is why DFT is commonly called an *ab initio* method as opposed to HF, in which the approximation that the wavefunction is assumed to be a single determinant is introduced right at the start. Searching for an accurate approximation for E_{XC} and V_{XC} is therefore a key part of the development of DFT.

3.2.4 Approximations to the exchange-correlation functional

In general, the exchange-correlation functional E_{XC} is separated into an exchange contribution E_{X} , representing interactions between electrons of the same spin, and a correlation contribution E_{C} , representing interactions between electrons of opposite spin. There are several categories of approximations to E_{XC} , described as follows.

Local density approximation

The local density approximation (LDA) is the simplest way to model E_{XC} . It assumes that E_{XC} per electron at position $\mathbf{r}$, $\epsilon(\mathbf{r})$, is equal to the corresponding value for a homogeneous electron gas that has the same density as $\mathbf{r}$, $\epsilon_{\text{XC}}^{\text{hom}}[n(\mathbf{r})]$. This implies that E_{XC} can be written as

$$E_{\text{XC}}[n(\mathbf{r})] = \int d\mathbf{r} \epsilon_{\text{XC}}^{\text{hom}}[n(\mathbf{r})]n(\mathbf{r}). \quad (3.51)$$

The form of the exchange functional for the uniform electron gas was determined by Dirac to be [128]:

$$E_{\text{X}}^{\text{LDA}}[\rho] = -\frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3} \int \rho^{4/3} d\mathbf{r}. \quad (3.52)$$

The functional for correlation cannot be determined from first principles and has been derived instead from Monte Carlo simulations of the uniform gas. Widely used LDA correlation functionals include the Vosko-Wilk-Nusair (VWN) [129] and Perdew-Wang (PW92) [130] functionals. The LDA approximation was the workhorse during early applications of DFT in solid state physics and is still widely used today. Despite its simple form, the LDA reliably reproduces properties such as geometries, elastic moduli and relative phases stabilities. However, the LDA significantly overbinds molecules

and lattices, underestimates band gaps, yields inaccurate binding energies and fails to describe van der Waals interactions.

Generalised gradient approximation

The generalised gradient approximation improves upon the LDA by including dependence on the gradient of the electron density as well as the local density in the exchange-correlation functional. The general form of E_{XC} under the GGA can therefore be written as:

$$E_{XC}[n(\mathbf{r})] = \int d^3r \epsilon_{XC}^{\text{hom.}}[n(\mathbf{r})]n(\mathbf{r}) + \int d^3r F_{XC}^{\text{hom.}}[n(\mathbf{r}), |\nabla n(\mathbf{r})|]. \quad (3.53)$$

There are two main schools of thought in the development of exchange functionals under the GGA. The first is a “first principles” approach based on quantum mechanical principles in which the functionals obey various physical properties, scaling relations and sum rules. Well known functionals based on this approach are Becke88 (B) [131] and Perdew-Wang (PW) [132]. The second is an empirical approach in which the functionals are parameterised using numerical fitting procedures to accurately reproduce experimental properties. Well known functionals based on this approach include Becke86 (B86) [133] and Perdew-Burke-Ernzerhof (PBE) [134]. Similar to the LDA, the development of correlation functionals under the GGA has been more complex. Two established GGA correlation functionals are Lee-Yang-Parr (LYP) [135] and PBE [134]. Compared to LDA, GGA gives a marked improvement in properties such as atomisation energies, structural energy differences and energy barriers. The improvement of GGA over LDA led to widespread acceptance of DFT in computational chemistry. However, like the LDA, GGA fails to describe van der Waals interactions and significantly underestimates band gaps. In addition, the accuracy of GGA is insufficient to correctly describe many chemical aspects of molecules. In addition, there is a large variation in accuracy between GGA functionals themselves thus careful comparison against experimental data is important to ensure robustness of calculations.

Meta-GGAs provide a further improvement in atomisation and binding energies compared to GGAs through inclusion of higher order derivatives of the electron density. However, the development of such functionals is more technically challenging due to numerical stability issues [136].

Hybrid functionals

The development of hybrid functionals were inspired by Becke's idea that the functional should contain some HF exchange based on the adiabatic connection. As the amount of HF exchange that should be included cannot be deduced from first principles, experimental data is typically used to parameterise the proportional contributions of different components of hybrid functionals.

One of the most well known hybrid functionals is the Becke 3 parameter Lee-Yang-Parr (B3LYP) hybrid functional [135, 137], which has the following composition

$$E_{XC}^{B3LYP} = E_{XC}^{LDA} + 0.2(E_X^{HF} - E_X^{LDA}) + 0.72(E_X^{B88} - E_X^{LDA}) + 0.81(E_C^{PW91} - E_C^{LDA}), \quad (3.54)$$

where E_X^{B88} is Becke's B88 exchange functional while E_C^{PW91} is the PW91 correlation functional. The coefficients of B3LYP were fitted to experimental atomisation energies, ionisation potentials, and electron and protons affinities for a set of atomic and molecular species. Other well established hybrid functionals include PBE0 [138, 139] and Heyd-Scuseria-Ernzerhof (HSE) [140].

Compared to the best GGA functionals, hybrid functionals give more reliable atomisation enthalpies, geometries and vibrational frequencies. In addition, band gaps from hybrid functionals are as accurate with those obtained with sophisticated correlated methods [64]. Due to its remarkable performance for a wide range of materials at a reasonable computational cost, the B3LYP functional is currently most commonly used out of all functionals. Although, it should be noted that B3LYP performs poorly for metals and small gap materials due to significant underestimation of formation energies and overestimation of lattice constants [141].

3.2.5 DFT in practice

The Kohn-Sham approach to DFT involves solving the Kohn-Sham equations, a complicated set of coupled equations containing both differentials and integrals. Most implementations of Kohn-Sham DFT make use of a scheme devised by Roothaan for the HF approach [142], in which the Kohn-Sham molecular orbitals are expanded as linear combinations of a set of predefined basis functions, η_μ :

$$\phi_i = \sum_{\mu=1}^L c_{\mu i} \eta_\mu, \quad (3.55)$$

where $c_{\mu i}$ are the coefficients of the expansion. The basis functions are collectively called the basis set. This is the linear combination of atomic orbitals (LCAO) approach, though despite the name, basis functions do not necessarily represent atomic orbitals. The LCAO approach transforms the originally non-linear optimisation problem into a linear optimisation problem where the unknown variables are the coefficients of the basis functions, $c_{\mu i}$. This results in the matrix equation

$$\mathbf{F}^{\text{KS}} \mathbf{C} = \mathbf{S} \mathbf{C} \boldsymbol{\epsilon}. \quad (3.56)$$

Here, $\mathbf{F}^{\text{KS}}$ is the Kohn-Sham matrix, with elements

$$F_{\mu\nu}^{\text{KS}} = \int \eta_{\mu}(\mathbf{r}) \hat{f}^{\text{KS}} \eta_{\nu}(\mathbf{r}) d\mathbf{r}, \quad (3.57)$$

where $\hat{f}^{\text{KS}}$ is the Kohn-Sham one-electron operator. $\mathbf{S}$ is the overlap matrix with elements

$$S_{\mu\nu} = \int \eta_{\mu}(\mathbf{r}) \eta_{\nu}(\mathbf{r}) d\mathbf{r}. \quad (3.58)$$

$\mathbf{C}$ is the matrix containing the coefficients of the basis functions in all eigenfunctions. $\boldsymbol{\epsilon}$ is a diagonal matrix of the orbital energies. All the matrices are $L \times L$ in dimension, where L is the number of basis functions.

In practice, some of the components of Kohn-Sham matrix elements, such as the four-centre Coulombic repulsion term, are computationally intensive due to the sheer number of integrals that need to be computed. Many codes therefore employ special strategies that use efficient techniques to make the computational cost manageable. An iterative approach is used following an initial guess to self-consistently obtain the eigenfunction coefficients and hence the wavefunction. This is the self-consistent field (SCF) procedure.

Basis sets

In Kohn-Sham DFT, a basis set, consisting of a set of mathematical functionals, is used to express the Kohn-Sham orbitals. There are two main categories of basis sets used: localised functions and plane waves.

As the wavefunction and hence the charge density are concentrated locally around atoms, it is intuitive to use a basis set composed of localised basis functions. Slater-type

orbitals (STOs) are exponentials with the typical form:

$$\eta^{\text{STO}} = Nr^{n-1}\exp[-\zeta r]Y_{lm}(\Theta, \phi), \quad (3.59)$$

where n is the principle quantum number, ζ is called the orbital exponent and Y_{lm} is a spherical harmonic. STOs are a natural choice for localised basis functions as their mathematical forms match the eigenfunctions of the hydrogen atom. In particular, they reproduce the cusp behaviour of a discontinuous derivative at the limit $r \rightarrow 0$ and also exhibit the correct exponential decay for large r . The problem with STOs is that for Coulomb integrals, and other many-centre integrals, computationally expensive numerical methods have to be employed as analytical techniques cannot be used. Consequently, modern quantum chemistry codes using localised basis sets do not use STOs. Instead, Gaussian-type orbitals (GTOs) are almost universally used. GTOs have the following form:

$$\eta^{\text{GTO}} = Nx^l y^m z^n \exp[-\alpha r^2], \quad (3.60)$$

where N is a normalisation factor and α is a orbital exponent representing the diffusivity of the basis function. The sum of the integer exponents $L = l + m + n$ gives the type of GTO. For example, a GTO is an s -function if $L = 0$, a p -function if $L = 1$ and so on. The reason why GTOs are ubiquitously used is because efficient algorithms are available to calculate the large number of four-centre-two-electron Coulomb (or exchange for HF methods) integrals. The downside of GTOs is that unlike STOs they do not reproduce the correct asymptotic behaviour. However, this can be improved by using contracted Gaussian functions (CGFs), which are a linear combination of several (usually between 3 and 6) GTOs, expressed as:

$$\eta_{\tau}^{\text{CGF}} = \sum_a^A d_{a\tau} \eta_a^{\text{GTO}}, \quad (3.61)$$

where $d_{a\tau}$ are the contraction coefficients, which can be chosen such that the overall CGF is like a single STO. Contraction of primitives also has the benefit of reducing the computational cost.

The simplest basis set, called a minimal set, uses only one basis function (can be contracted or not) for each atomic orbital up to and including the valence orbitals. An example is the STO-3G basis set, where each basis function is a CGF that is a contraction of three primitive GTO functions. For carbon, this basis set is formed of five basis functions, two for the $1s$ and $2s$ orbitals and three representing the orbitals

in the $2p$ shell (p_x , p_y and p_z). Because it has so few basis functions, a minimal basis set can only reproduce qualitative results and so are only used to obtain rough initial geometries during optimisation.

The minimal basis set is improved by including more than one basis function for some or all atomic orbitals. For example, double-zeta basis sets include two basis functions for each atomic orbital, triple-zeta basis sets include three basis functions for each atomic orbital, and so on. Split-valence basis sets include only one basis function for each core atomic orbital, and multiple basis functions for the valence atomic orbitals. To ensure that the core part of the wavefunction is accurately described, the core orbital usually consists of a significant number of CGFs. Split-valence basis are more commonly used compared to n -zeta basis sets as they retain the accuracy of the (chemically active) valence orbitals while having fewer basis functions.

Diffuse functions with a large Gaussian exponent are sometimes included in the basis set of certain atoms. This allows better description of the wavefunction away from nuclei and so are usually necessary for anions as they are highly polarisable. In addition to functions describing valence orbitals, Functions of higher angular momentum, called polarisation functions, can be added in addition to the functions describing valence atomic orbitals. For example, for carbon atoms, the polarisation functions would describe d -orbitals. As polarisation functions have more angular nodal planes than functions of the valence orbitals, this allows for better description of asymmetry, which may be beneficial depending on the molecular environment that the orbitals are in.

The notation by Pople is commonly used to denote a basis set. For example, the basis set 6-311G is a split basis set with one CGF for core orbitals consisting of 6 GTOs, and 3 CGFs for valence orbitals which consist of 3, 1 and 1 GTOs. Diffuse functions and polarisation functions are denoted by the addition of ‘+’ and ‘*’, respectively, to the name of the basis set (e.g. 6-311+G*). Generally, the more basis functions included, the better the accuracy of the calculation, albeit at a higher computational cost. The choice of the basis set is therefore a compromise between accuracy and computational expense.

Plane waves, the other main type of basis functions, are solutions of the Schrödinger equation of a free particle. They have the following general form:

$$\eta^{\text{PW}} = \exp[i\mathbf{k}\mathbf{r}], \quad (3.62)$$

where $\mathbf{k}$ is the wave vector. As plane waves extend throughout all space, they are often

used in periodic calculations where Bloch's theorem is used to express each electronic wavefunction, ψ_i , of the infinite system as wavefunctions at reciprocal space vectors, $\mathbf{k}$, of a Bravais lattice:

$$\psi(\mathbf{r}) = \sum_{\mathbf{G}} c_{i,\mathbf{k}+\mathbf{G}} \exp[i(\mathbf{k} + \mathbf{G}) \cdot \mathbf{r}]. \quad (3.63)$$

Here, $\mathbf{G}$ are reciprocal lattice vectors defined by the relation

$$\mathbf{G} \cdot \mathbf{l} = 2\pi m, \quad (3.64)$$

where $\mathbf{l}$ is a lattice vector and m is an integer. Each plane wave $\exp[i(\mathbf{k}+\mathbf{G}) \cdot \mathbf{r}]$ has coefficient $c_{i,\mathbf{k}+\mathbf{G}}$ and a kinetic energy of $(\hbar^2/2m)|\mathbf{k}+\mathbf{G}|^2$. A larger kinetic energy represents a plane wave with a smaller wavelength. A plane wave basis set is specified by a cutoff energy such that all plane waves with a kinetic energy less than the cutoff is included in the set.

Compared to localised basis sets, a significantly larger number of basis functions are normally required to achieve the same level of accuracy when using plane wave basis sets. This is because core electrons are concentrated close to atomic nuclei, which results in large density gradients. Consequently, plane waves with small wavelengths, equivalent to large kinetic energies, are required to give an accurate description of the core electron density. To mitigate the computational expense due to the large number of basis functions, effective core potentials, also called pseudopotentials, are often employed to represent the core region. This is the *plane wave pseudopotential* (PWPP) approach. In the PWPP approach, relatively few basis functions are needed as the plane waves are only used to describe the valence electron density.

3.2.6 Periodic DFT

It may seem that the study of the electronic structure and properties of a crystal is an impossible task due to the sheer number ($\sim 10^{23}$) of atoms. However, the problem can be made tractable by taking advantage of translational symmetry of crystals. In real space, also called direct space, a crystal is characterised by a unit cell with basis vectors $\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$ such that any two points joined by a vector

$$\mathbf{g} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3 \quad (3.65)$$

with integral coefficients n_1 , n_2 and n_3 , are equivalent. A system with this property is also said to be translationally invariant. Given a unit cell, the infinite crystal lattice,

referred to as the direct lattice, can then be constructed by applying three-dimensional periodic boundary conditions (3D PBC), in other words by repeating the unit cell infinitely along all three dimensions. Other types of systems such as surfaces (2D) or a polymer (1D) are similarly modelled by applying PBCs along fewer dimensions. In the rest of this section, 3D PBCs will be assumed.

The Fourier transform of the direct lattice gives the so-called reciprocal lattice, which is said to exist in reciprocal space. The reciprocal lattice is also characterised by the reciprocal basis vectors $\mathbf{b}_1$, $\mathbf{b}_2$ and $\mathbf{b}_3$ which are connected to the basis vectors in direct space via the following equations:

$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\Omega} \quad (3.66)$$

$$\mathbf{b}_2 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\Omega} \quad (3.67)$$

$$\mathbf{b}_3 = 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\Omega} \quad (3.68)$$

where

$$\Omega = \mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3) \quad (3.69)$$

gives the volume of the unit cell in direct space. Similar to direct space, the linear combination of $\mathbf{b}_1$, $\mathbf{b}_2$, $\mathbf{b}_3$:

$$\mathbf{K} = K_1 \mathbf{b}_1 + K_2 \mathbf{b}_2 + K_3 \mathbf{b}_3 \quad (3.70)$$

with integer coefficients K_1 , K_2 and K_3 , gives reciprocal lattice vectors that connect equivalent points in reciprocal space. The reciprocal basis vectors can be used to define a unit cell in reciprocal space. One common and useful way to do this is to consider one reciprocal lattice point and its nearest equivalent points in the reciprocal lattice. A unit cell, known as the *first Brillouin zone*, is then the volume containing all points closer to the lattice point than to any other equivalent points.

The concept of a reciprocal lattice is very useful, both experimentally and in DFT. In neutron and X-ray diffraction, the diffraction pattern of a crystal gives the reciprocal vectors of the lattice, which can be used to deduce the crystal structure. The reciprocal lattice is also the basis of Bloch's theorem of waves in the periodic lattice, which states that given a potential invariant with respect to translation by any direct lattice vector $\mathbf{g}$:

$$V(\mathbf{r} - \mathbf{g}) = V(\mathbf{r}), \quad (3.71)$$

the eigenfunctions ϕ , called Bloch functions, satisfy the following

$$\phi(\mathbf{r} + \mathbf{g}; \mathbf{k}) = e^{i\mathbf{k} \cdot \mathbf{g}} \phi(\mathbf{r}; \mathbf{k}), \quad (3.72)$$

where $\mathbf{k}$ is any reciprocal lattice vector. This implies that a Bloch function can be written as:

$$\phi(\mathbf{r}; \mathbf{k}) = e^{i\mathbf{k} \cdot \mathbf{r}} u(\mathbf{r}; \mathbf{k}), \quad (3.73)$$

where $u(\mathbf{r}; \mathbf{k})$ is a periodic function with the same periodicity of the lattice. Equation 3.72 is verified as shown below:

$$\phi(\mathbf{r} + \mathbf{g}; \mathbf{k}) = e^{i\mathbf{k} \cdot (\mathbf{r} + \mathbf{g})} u(\mathbf{r} + \mathbf{g}; \mathbf{k}) = e^{i\mathbf{k} \cdot \mathbf{g}} e^{i\mathbf{k} \cdot \mathbf{r}} u(\mathbf{r}; \mathbf{k}) = e^{i\mathbf{k} \cdot \mathbf{g}} \phi(\mathbf{r}; \mathbf{k}). \quad (3.74)$$

For a infinite lattice, the number of possible k points in the first Brillouin zone, or any reciprocal unit cell, is also infinite. Thus, k can be considered a continuous variable.

In a periodic system, there are an infinite number of atoms, which means that the Hamiltonian matrix in direct space is infinitely large. However, by working in reciprocal space and using a basis set comprised of a finite number of Bloch's functions, the original problem of infinite size is transformed via Bloch's theorem into an infinite number of matrix problems with finite-sized matrices, each associated with an individual k point within the first Brillouin zone. The step that makes the problem tractable is the application of k point sampling, which is to only consider a small set of appropriately chosen k points. This is justified as eigenfunctions and eigenvalues change smoothly with respect to k . The Bloch functions used in the basis set can take the form of localised atomic orbitals or plane waves, which were both described in Section 3.2.5.

3.3 QM/MM

For a large system, such as an enzyme, which consists of thousands of atoms or more, it is often unfeasible to model its chemical properties using a single standard computational method. QM methods such as DFT and HF can achieve the necessary accuracy, but the large number of atoms in the system makes calculations impractical due to high computational cost. On the contrary, computational expense is not an issue for an MM approach, but with the exception of (carefully parameterised) reactive force fields, sufficient accuracy cannot be achieved. The hybrid Quantum Mechanics/Molecular Mechanics (QM/MM) approach, first introduced in the seminal paper by Warshel and Levitt published in 1976, makes such problems tractable by combin-

ing the accuracy of QM with the computational efficiency of MM [143]. In the 1990s, the QM/MM approach underwent rapid development, leading to its widespread acceptance and use. Today the QM/MM approach is mainly applied to model reactions in organometallic or biomolecular systems, but it is also becoming increasingly important in chemical calculations of inorganic systems [144]. In this section, an overview of the QM/MM methodology, including its theory, capabilities, limitations and implementation, is given.

QM/MM basics and terminology

In a standard QM/MM approach, the system is partitioned into a small region containing the chemically interesting part of the system and the rest of the system representing the surrounding environment, these are the “inner” (I) and “outer” (O) regions respectively. The inner region is modelled using (QM) electronic structure methods such as DFT. The outer region is modelled using computationally cheap classical (MM) force field based methods. The inner and outer regions are also commonly referred to as the QM and MM regions respectively; these terms are henceforth used interchangeably.

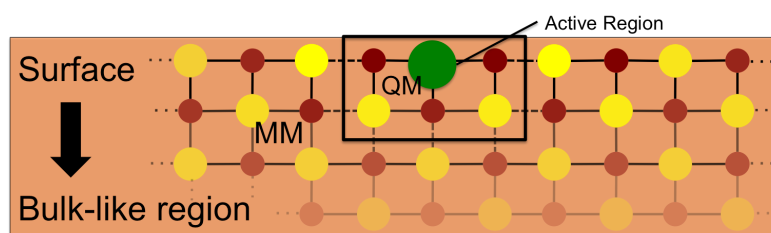


Figure 3.8: Illustration of a surface modelled using a QM/MM approach.

An illustration showing an example QM/MM setup in a surface system is shown in Figure 3.11. Despite the compromise of modelling the outer region, which constitutes most of the whole system, using classical methods, the QM/MM approach in principle enables the chemistry of the system to be studied at a reasonable computational cost without significant loss of accuracy compared to a pure QM approach. The boundary between the QM and MM regions, referred to here as the “QM-MM boundary”, need to be carefully treated to ensure that calculations are robust enough. Key issues that need to be considered in a QM/MM calculation are:

1. Calculation of the QM/MM energy
2. Choice of the QM and MM methods

3. Partitioning of the system into QM and MM regions and treatment of the boundary region

These issues are discussed in detail in Section 3.3.1 to 3.3.3.

3.3.1 The QM/MM energy

As with pure MM methods and electronic structure methods, calculation of the total system energy is fundamental to QM/MM methods. The calculation of the total energy of the system, $E_{\text{QM/MM}}$, can be classified into additive or subtractive schemes, which differ in the way the interaction energy between the inner and outer regions is treated.

The additive scheme

In the additive scheme, the total energy of the system is:

$$E_{\text{QM/MM}}^{\text{add.}} = E_{\text{QM}}(\mathbf{I}) + E_{\text{MM}}(\mathbf{O}) + E(\mathbf{I}, \mathbf{O}) , \quad (3.75)$$

$E_{\text{QM}}(\mathbf{I})$ is the energy of the inner region calculated at the QM level of theory, $E_{\text{MM}}(\mathbf{O})$ is the energy of the outer region at the MM level of theory and $E(\mathbf{I}, \mathbf{O})$ is the explicit coupling term representing the energy of the interaction between the inner and outer regions. In general, the coupling term has three components:

$$E(\mathbf{I}, \mathbf{O}) = E_{\text{MM}}^{\text{bond}} + E_{\text{MM}}^{\text{vdW}} + E^{\text{Coulomb}} , \quad (3.76)$$

where $E_{\text{MM}}^{\text{bond}}$ is the energy of bonded terms (bond stretching, angle bending, torsional etc.) representing interactions that span across the boundary of the inner and outer regions, $E_{\text{MM}}^{\text{vdW}}$ is the energy of van der Waals interactions between the atoms in the inner region and atoms in the outer region, and E^{Coulomb} is the electrostatic (Coulomb) energy between atoms in the inner region and atoms in the outer region. In general, the first two terms are both calculated at the MM level of theory. Additive QM/MM approaches can be further differentiated into two schemes based on how the electrostatic interaction term is calculated. In the electrostatic embedding scheme, the electrostatic interaction energy is calculated at the QM level of theory by including one-electron operators in the QM Hamiltonian during calculation of the inner region. This usually involves using atom-centred point charges to represent the MM atoms in the QM Hamiltonian. Methods using more complicated representations such as distributed multipoles instead of point charges have also been developed [145, 146]. In the mechanical embedding scheme, the electrostatic interaction energy, like other cross-region interaction terms,

is calculated at the MM level of theory. Here, the atoms of the inner region usually appear as point charges in the MM calculation of the outer region.

The advantage of mechanical embedding lies in its simplicity. On the downside, it may be difficult to obtain accurate electrostatic MM parameters (usually partial charges) of the inner region. Furthermore, polarisation of the electronic structure of the inner region due to the outer region is ignored, which may significantly compromise accuracy of the inner region. The advantages of electrostatic embedding is that no MM parameters are needed for the inner region and that the electronic structure of the inner region is able to respond to the outer region. However, an appropriate charge distribution needs to be constructed to represent the outer region. In addition, the inclusion of the charge distribution of the outer region in the QM calculation means the computational cost is higher compared to mechanical embedding. While the polarisation of the inner region due to the outer region is modelled in electrostatic embedding, the polarisation of the outer region due to the inner region is not modelled. This has led to the development of polarised embedding schemes, which employ a polarisable force field for the outer region that can respond to perturbation by an external field. In polarised embedding calculations, the inner and outer regions polarise each other until self-consistency of their charge distributions is achieved. Common polarisable force field models include, the shell model of Dick and Overhauser [119], introduced in Section 3.1.1, the charge-on-spring model [147] and the Drude oscillator model [148].

The subtractive scheme

In the subtractive scheme, the total energy is:

$$E_{QM/MM}^{\text{sub.}} = E_{\text{MM}}(\mathbf{I}, \mathbf{O}) + E_{\text{QM}}(\mathbf{I}) - E_{\text{MM}}(\mathbf{I}) , \quad (3.77)$$

where $E_{\text{MM}}(\mathbf{I}, \mathbf{O})$ is the energy of the entire system at the MM level of theory while $E_{\text{QM}}(\mathbf{I})$ and $E_{\text{MM}}(\mathbf{I})$ are the energies of the inner system calculated at the QM and MM levels of theory respectively. The subtraction of the final term, which gives the subtractive approach its name, avoids double counting of the energy of the inner region.

The subtractive QM/MM scheme can be interpreted as an MM approach where the inner region has been cut out and treated at the QM level of theory. As the interaction between the inner and outer regions is modelled implicitly in the MM calculation of the whole system, no explicit coupling terms are needed. This means that compared to the additive scheme, the subtractive scheme is easier to implement as the QM and MM procedures do not need to be modified. However, a complete set of MM parameters,

including both bonded and non-bonded terms, are required for the inner region, which may be hard to obtain. In addition, the subtractive scheme is not suitable for studies that involve chemical reactions as MM parameters of the inner region are static. As the coupling between the regions is modelled at the MM level of theory, similar to mechanical embedding in additive schemes, the electrostatic interaction between the inner and outer regions may be poorly described.

Some examples of QM/MM approaches which use the subtractive scheme are the ONIOM [149,150] and IMOMM [151] methods developed by Morokuma and co-workers.

3.3.2 Choice of methods

The QM/MM framework in principle admits any combination of QM and MM methods. In this section the factors that influence the choice of methods are discussed.

As in a pure QM approach, the choice of the QM method for a QM/MM study requires an appropriate balance to be struck between accuracy and computational effort. Semiempirical QM methods such as AM1 and PM3 have traditionally been popular choices, particularly for QM/MM molecular dynamics (MD) simulations, which incur high computational expense due to the large number of energy evaluations required. However, these are not applicable to all systems due to lack of parameters. A higher level of accuracy can generally be obtained by using DFT or molecular orbital methods such as MP2 and coupled-cluster methods. In the case of electrostatic embedding, one restriction on the choice of QM method is that the method must be able to accommodate a set of external point charges.

The MM force fields chosen for a QM/MM study must be able to accurately describe the outer region *in addition* to its interactions with the inner region. Universal force fields such as CHARMM27, AMBER and OPLS-AA, which have parameters for all atoms, are commonly used in studies of biomolecular systems.

3.3.3 Partitioning of the system

Defining the QM-MM boundary

A minimum size of the QM region can be first determined from chemical intuition, as the chemically active region must obviously be included in the QM region. To ensure accuracy, the size of the QM region should be sufficiently large such that the properties of the QM region, such as the geometry and electronic structure, are converged with respect to its size. The definition of the QM region in turn implicitly defines the MM region. Conventionally, once the QM/MM partitioning has been defined, it is fixed

for the whole duration of the study. However, this is ill-suited for studies where the active site moves during geometry optimisation or MD calculations. For such cases, flexible partitioning schemes are employed, where the QM/MM boundary dynamically shifts with the active site. Several algorithms have been developed for simulations in the liquid-state based on the introduction of a buffer region between QM and MM regions [152, 153]. Smooth functions are typically employed to avoid discontinuities in the force as a solvent molecule moves between regions. Another flexible partitioning scheme is the ‘learn-on-the-fly’ (LOTF) scheme of Csányi *et al.*, which has been used to study crack propagation in a solid [154]. In addition to dynamical partitioning of the system, the LOTF scheme uses force-mixing techniques to propagate the classical potential during the simulation, which ensures conservation of momentum during MD.

Treatment of the boundary

For QM/MM studies of molecular systems, it is straightforward to define partitioning such that the QM/MM boundary does not cut through any bonds. However, for other systems, such as ionic surfaces and large biomolecules, it is inevitable that the QM/MM boundary cuts across bonds. Careful treatment of the boundary is vital to ensure that the resulting undercoordination of QM boundary atoms does not severely impact the accuracy. The ideal approach to handle the QM-MM boundary depends on the type of bonding at the boundary.

For covalent systems such as enzymes and zeolites, there are two main classes of boundary treatments aimed at capping dangling bonds to satisfy the valency of boundary QM atoms. The first is the link atom approach, where additional atoms that are not part of the real system are placed near the boundary to restore the covalency of boundary QM atoms. The additional atoms, called link atoms, are normally hydrogen atoms. The link atom scheme is easy to implement, but may not reproduce the correct electronic structure at the QM-MM boundary. Improvements to the basic link atom scheme can be made by using effective core potentials parameterised to mimic the properties of the original cut bonds [155, 156]. Parameterised ECPs can reproduce more accurate results compared to the basic link atoms, but can be hard to implement as parameters are only available for certain bonds.

The second class of boundary treatments in covalent systems is the localised-orbital approach, where hybrid orbitals are placed at the boundary region. One example is the local self-consistent field (LSCF) algorithm, in which strictly localised bond orbitals (SLBOs), obtained from calculations on small model compounds, are used to represent

cut bonds [157,158]. To prevent admixture with other QM basis functions, the SLBOs are excluded from the SCF procedure of the QM calculation. Another example of the localised-orbital approach is the generalised hybrid orbital (GHO) method, in which a set of hybrid orbitals is assigned to each MM boundary atom [159,160]. The type of hybrid orbitals used (e.g. sp^3) depends on the local geometry and bonding at the boundary. The set of hybrid orbitals consists of an active orbital that is directed to the boundary QM atom, and auxiliary orbitals that form the remainder. While all hybrid orbitals are included in the QM calculation, only the active hybrid orbital participates in the SCF procedure.

Each type of boundary treatment has its advantages and disadvantages. The link atom approach is simple to implement and hence widely used. However, artificial link atoms complicate the evaluation of the system energy and introduces extra degrees of freedom that make geometry optimisations more difficult. In addition, the short distance between a link atom and its corresponding boundary MM atom, which appear as a point charge in the QM calculation, can result in unphysical polarisation of the bond between the link atom and the QM atom. This overpolarisation problem can be alleviated by using a charge shifting scheme, which shifts charge away from boundary MM atoms to other MM atoms connected to them [161]. The localised orbital approach is fundamentally more robust than the link atom approach as the charge distribution at the QM-MM boundary is described quantum mechanically. The overpolarisation problem which can occur when using link atom methods is also avoided due to the delocalised representation of charges. However, compared to link atoms methods, localised orbital methods are more technically involved as more careful parameterisation is required. In addition, the parameters are generally not transferable if the underlying MM or QM methods are changed. Despite its relative simplicity, the link atom approach can achieve similar accuracy compared to the localised orbital approach [162].

For ionic systems, such as metal oxides, link atoms or other valence capping schemes are not necessary as no covalent bonds are broken by the QM-MM boundary. However, delocalisation of electrons from the QM boundary atoms into the MM region may be an issue; this can be prevented by placing large core pseudopotentials on boundary MM atoms surrounding the QM region. French *et al.* employed this strategy in a study on the growth of Cu Clusters on the (0001)-ZnO surface [163].

3.3.4 Implementation of QM/MM

There are three main ways of implementing QM/MM methods computationally:

1. Extension of a QM code. The MM environment is incorporated as a perturbation. Examples include **Gaussian**, which implements the ONIOM method, and the **ADF** [164] and **GAMESS-UK** [165] packages.
2. Extension of an MM code. The QM code is included as a force-field extension. One example is the **AMBER** [166] package.
3. A separate code that interfaces with existing QM and MM codes and has its own routines to drive tasks such as energy calculations, geometry optimisation and molecular dynamics. Examples include the **ChemShell** [167, 168] and **QMMM** [169] packages.

3.4 Modelling surfaces

Previously, various theoretical approaches to calculate the total energy of a system were discussed. As the aim of this project is to study chemical processes occurring on a surface, it is also important to discuss technical aspects relevant to surface modelling. First, Tasker’s classifications, which are used to identify potentially stable surfaces of the CuFeS_2 system in Chapter 5) are introduced. Second, two different models of surface representation, the slab and cluster models, which are both employed in this project, are described.

3.4.1 Tasker’s classifications and the stability of ionic surfaces

There are an infinite number of planes that can be cut to create a surface from a crystal. Tasker provided a way of classifying ionic surfaces into three types:

- Type 1: Surfaces with neutral atomic layers that share the same stoichiometry of the host crystal
- Type 2: Surfaces with charged atomic layers arranged in a symmetrical fashion such that the repeating unit has no net electrostatic dipole moment perpendicular to the surface.
- Type 3: Surfaces with charged atomic layers with an arrangement such that there is a net electrostatic dipole moment perpendicular to the surface.

The three different Tasker surface types are illustrated in Figure 3.9. Type 1 and 2 surfaces are referred to as nonpolar surfaces while type 3 surfaces are referred to as

polar surfaces. Tasker’s analysis concluded that polar surfaces have a diverging surface energy and are unlikely to exist unless stabilised in some way to remove the macroscopic field. On the contrary, nonpolar surfaces may exist with limited reconstruction. As a general rule of thumb, most surfaces of ionic crystals are polar in nature while those which are nonpolar are likely to have small Miller indices (“low-index surfaces”). If the partial charges of atoms in the surface are known the electrostatic dipole moment can be readily calculated. Tasker’s classification thus provides a simple way to screen for potentially stable surfaces.

It should be stressed that the key quantity that determines the stability of a surface is the surface excess charge, as an infinite surface would have an infinite surface energy. Even if a surface excess charge is compensated by an equal and opposite charge on the opposing surface of a slab, the surface energy is not well defined as it increases linearly with slab thickness due to the internal electrostatic field. A polar slab can therefore only achieve a non-diverging surface energy if the surface excess charge is completely removed via charge transfer or other mechanisms.

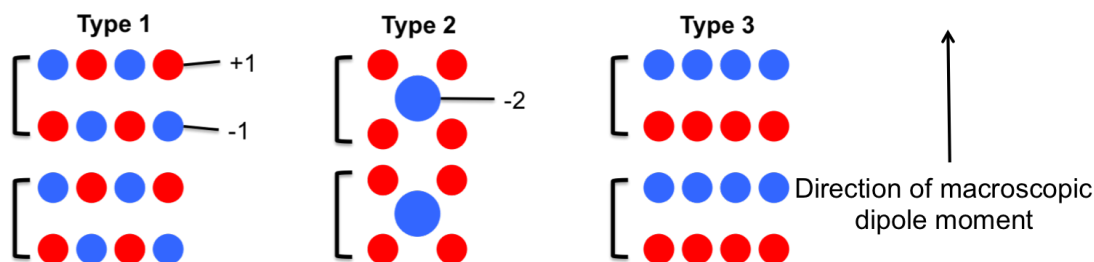


Figure 3.9: Tasker’s classifications of ionic surfaces. Blue ions are negatively charged while red ions are positively charged.

3.4.2 Surface models

In computational chemistry and material science, there are two main ways to represent a surface in a calculation: the slab model and the finite cluster model. In the slab model, the surface is represented by a slab of finite thickness, and bound by two surfaces, which may be related by symmetry. In general, the slab thickness should be thick enough such that geometric and energetic properties are converged with respect to slab thickness. In real calculations, either 2D or 3D PBCs are imposed to handle a slab. In the 2D slab model, the unit cell is two dimensional, implying that the slab is periodic in the dimensions of the surface plane and not in the direction perpendicular to the surface.

In the 3D slab model, the slab is periodic in all dimensions and the slabs are separated by a vacuum region of finite thickness. The vacuum region must be made large enough to prevent spurious interactions between slab from significantly affecting the accuracy of the calculation. The 3D slab model is also referred to as the slab supercell model. For electronic structure calculations that employ a plane wave basis set, a 3D slab model must be employed, as intermediate quantities such as charge density require a 3D Fourier representation. If a localised basis set is employed, either the 2D or 3D slab models can be used.

In the finite cluster model, the surface is represented by a finite cluster, which is usually hemispherical in shape with the flat part of the hemisphere corresponding to the surface of interest. Figure 3.10 shows the CuFeS₂ S-terminated ($\bar{1}\bar{1}2$) surface represented by both models.

The slab model is typically used for QM studies of surfaces due to its simplicity. However, the termination of the system at the spherical boundary results in cleaved bonds and hence undercoordinated boundary atoms. Consequently, the required system size of a finite cluster model is usually much larger than that for a slab model to ensure accurate description of the bulk environment. Due to its simplicity and computational efficiency, the slab model is preferred for QM studies of surfaces. However, if the system includes localised features such as defects, a finite cluster model may be more suitable, to prevent spurious interactions arising from periodicity. Alternatively, a slab model with a larger surface unit cell can be used to reduce unwanted periodic interactions. For hybrid QM/MM calculations with electrostatic embedding, the finite cluster model is often the only feasible model as many QM codes are incapable of computing the interaction of the QM region with an infinite charge distribution.

To include the missing electrostatic effects of the bulk crystal missing due to truncation of the bulk, more advanced coupling or embedding techniques are required. In Section 3.5, several finite embedded cluster models are introduced. In particular, the theory and applications of the embedded finite cluster of Sokol *et al.*, which is the basis of the QM/MM methodology developed and tested in Chapter 6, is discussed in detail.

3.4.3 Surface energy and the Wulff construction

If the slab model is used, the surface energy is readily computed as

$$E_{\text{surf}} = \frac{E^n - nE_{\text{bulk}}}{2A}, \quad (3.78)$$

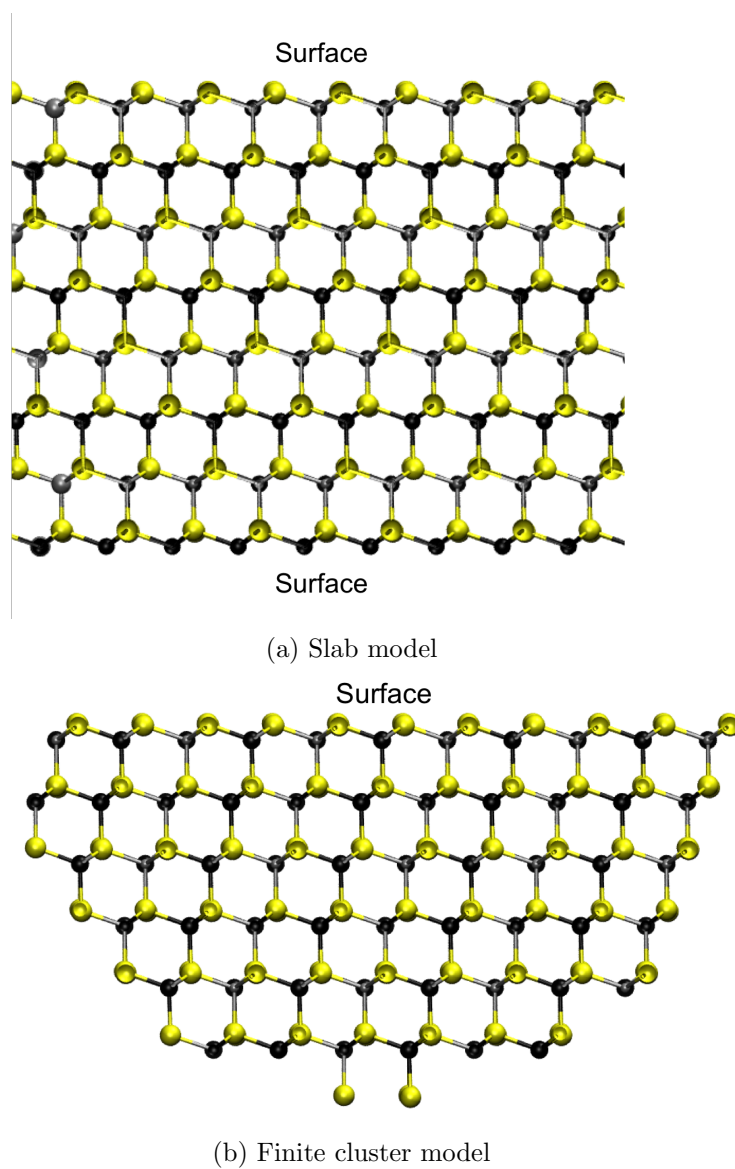


Figure 3.10: The slab (top) and cluster (bottom) models of representing a surface.

where E^n is the energy of the slab consisting of n atoms in the unit cell, E_{bulk} is the per atom energy of the bulk crystal, and A is the area of the surface unit cell. This relation assumes that the two surfaces of the slab are identical and that the slab is stoichiometric. The factor of $1/2$ accounts for the fact that a slab is bound by two surfaces.

Given the formation energy of a range of surfaces for a material, the Wulff construction can be used to determine the equilibrium crystal shape of that material. The method is based on the theory, first stated by Wulff [170] and later proved by von Laue [171], that a crystal constructed such that the distance from the centre of the crystal to the surface is proportional to the surface energy gives the crystal shape that minimises the total surface energy. The Wulff construction is thus a useful tool to predict the surface morphology of a material and hence determine the cleavage planes of a material.

3.5 The finite embedded cluster model

3.5.1 The classical Mott-Littleton approach

The general embedded cluster approach to model periodic systems has its conceptual origins in the method developed by Mott and Littleton to treat charged defects in dielectric materials [172]. In the classical Mott-Littleton approach, the crystal is partitioned into three regions centred about the defect. Region I and IIa are the inner and outer concentric spherical regions respectively while region IIb consists of the rest of the crystal. A key approximation in the model, called the Mott-Littleton approximation, assumes that the response of atoms far away from the defect is harmonic and is purely due to the polarisation caused by the defect. As ions in region I closely surround the defect they are assumed to be strongly perturbed strongly by the defect. These ions are therefore treated explicitly using short-range inter-atomic potentials and their positions are relaxed until equilibrium is reached. Conversely, the ions in region IIa are further away from the defect and hence assumed to only be weakly perturbed by it. The displacements of the ions in this region are therefore implicitly calculated through the Mott-Littleton approximation but interactions with ions in region I are still explicitly computed using inter-atomic potentials. The ions in region IIb, furthest away from the defect, are fixed geometrically and their interactions with region I are treated using the Mott-Littleton approximation.

In the Mott-Littleton approximation, the crystal polarisation, P , due to a defect

with charge q is given as

$$P = \frac{q}{4\pi r} \left(1 - \frac{1}{\epsilon}\right), \quad (3.79)$$

where r is the distance to the defect and ϵ is the electric permittivity. The contribution of polarisation due to individual displacements to the total energy is calculated by applying this equation over regions IIa and IIb.

Despite significant approximations applied, the Mott-Littleton approach has been shown to produce accurate defect energies and geometries as long as the inner region sizes are sufficiently large. With the development of higher level QM based techniques, the original Mott-Littleton approach has been adapted by many to enable more accurate calculations on finite clusters, both with and without embedding, at the QM and QM/MM levels.

3.5.2 QM and QM/MM approaches

The perturbed cluster approach by Pisani *et al.* was devised to study local defects in crystals at the Hartree-Fock level of theory and implemented in the **EMBED** code [173, 174]. In this approach the entire system is divided into a molecular cluster containing the defect and an outer region representing the rest of the crystal. A wavefunction is obtained for the molecular cluster in the crystal field of the outer region. The wavefunction for the latter is corrected based on the assumption that the density of states projected onto the outer region is the same as that of the perfect crystal, giving a new wavefunction. This is repeated until self-consistency is achieved. The perturbed cluster approach was used to study the heterolytic dissociation of hydrogen at a surface divacancy at the (001) MgO surface [175].

The cyclic cluster model with Madelung correction (CCMM) by Bredow *et al.* replaces the local environment of each cluster atom by that of a fictitious cyclic arrangement [176–178]. In the model, a linear one-dimensional chain of atoms is treated in the same way as a cyclic arrangement of the same number of atoms on a ring. This is extended to two and three dimensions through torus and hypertorus arrangements, respectively. All interactions for each atom are then calculated within its Wigner-Seitz cell. The long range Madelung potential correction is implemented in a self consistent manner using point charges placed at lattice sites whose charges are calculated from the cluster density matrix using a Löwdin population analysis. The CCMM methodology was employed in a study of bulk and surface properties for a variety of metal oxides [178]. Excellent agreement with experimental data was obtained for many properties such as structure parameters, binding energies, band gaps and charges. The

study also highlighted the importance of including the Madelung corrections, as without them poor convergence behaviour of binding and surface energies is exhibited with respect to cluster size.

Another cluster model is the emdded molecular cluster (EMC) model, developed by Kantorovich, which is based on the concepts of localised electron groups [179]. In the EMC model, a cluster is defined and the rest of the crystal is split into structural elements such that the wave function is localised within each structural element. Atoms in structural elements are represented by spherical non-point charges. The central idea of the EMC model is that the wave function of the whole system, which consists of the cluster and the remaining part of the crystal, is an antisymmetrised product of the wave function of the cluster and those of structural elements. The EMC accounts for Coulomb and exchange interactions between the cluster and the structural elements. However, the major drawback of the EMC model is that when applied to perfect, defect-free crystals in geometry optimisation calculations, displacement of boundary cluster atoms from their lattice sites is observed. In addition, the resulting electron density distribution on the boundary atoms is different to that of the original perfect crystal. These boundary effects can negatively affect the accuracy of the crystal response to polarisation of the cluster and result in incorrect energetics and geometric properties in the cluster. To reduce the boundary effects, Shidlovskaya adapted the EMC by employing a boundary region common for the wave functions of the cluster and that of the structural elements in the remainder of the crystal instead of a well-defined boundary to more accurately describe the interaction between cluster and structural elements [180].

3.5.3 The QM/MM approach by Sokol *et al.*

The final methodology described here is the embedded cluster QM/MM approach of Sokol *et al.*, which was devised specifically for the study of reactions at the surface of ionic solids including reconstructed polar surfaces [181]. This is highly relevant for studies of dissolution at the CuFeS₂ surface. Furthermore, the methodology is readily accessible through its implementation in the **ChemShell** code and is therefore chosen as the basis for the development and testing of a methodology tailored for future studies of chemical processes on the CuFeS₂ surface at solid-liquid interface. The methodology is described in detail here.

As with the localisation method by Kantorovich, a central region containing the active site is defined and the crystal remainder is divided into structural elements. The

central region is modelled at the QM level of theory, typically DFT, and is henceforth referred to as the QM region. Since this methodology assumes an ionic system, the wavefunction overlap between ions is small which means it is appropriate to define each individual ion as a structural element. The combined crystal remainder is typically modelled using classical pair potentials and the shell model and is henceforth referred to as the MM region.

The total energy can be partitioned into the sum of the self-energy of each structural element, which here is the single atom energy of all MM atoms, combined with the interaction energy expanded as a series over the number of interacting elements:

$$E^{\text{Total}} = E^{\text{self}} + E^{2\text{-body}} + E^{3\text{-body}} + E^{4\text{-body}} + \dots \quad (3.80)$$

The self energy contribution, E^{self} , consists of the on-site energy of the QM region and the sum of single atom energies of the MM region. The former, $E_{\text{QM}}^{\text{self}}$, is the expectation of the usual many-electron Hamiltonian, $\hat{H}^{\text{QM}}$, with the corresponding wave function, $|\Psi\rangle$, along with the sum of the electrostatic interaction energy between pairs of QM nuclei, $E_{ab}^{\text{electrostatic}}$:

$$E_{\text{self}}^{\text{QM}} = \langle \Psi | \hat{H}^{\text{QM}} | \Psi \rangle + \frac{1}{2} \sum_{a,b} E_{ab}^{\text{electrostatic}}. \quad (3.81)$$

Assuming a shell model treatment for the MM region, the latter is sum of the shell polarisation energies in the MM region. The general form of the energy due to polarisation of shell of the MM ion i consists of a harmonic and, optionally, a quartic term:

$$E_i^{\text{shell}} = \frac{1}{2!} k_i^{(2)} d_i^2 + \frac{1}{4!} k_i^{(4)} d_i^4, \quad (3.82)$$

where

$$d_i = |\mathbf{r}_i^{\text{shell}} - \mathbf{r}_i^{\text{core}}|. \quad (3.83)$$

The contribution of two-body terms, $E^{2\text{-body}}$, to the total energy is:

$$E^{2\text{-body}} = \sum_j E_{\text{QM},j} + \frac{1}{2} \sum_{i,j} E_{ij}. \quad (3.84)$$

The first term represents the energy due to interactions between the QM region and all structural elements in the MM region, modelled using electrostatic embedding. The energy due to interactions between the QM region and a single structural element j can be decomposed into the following:

$$E_{\text{QM},j} = \langle \Psi | \hat{V}_j^{\text{embedding}} | \Psi \rangle + \sum_a E_{aj}^{\text{nuc}}. \quad (3.85)$$

The first term on the right hand side represents the energy due to the effect of the embedding potential associated with MM ion j on the QM wavefunction and is further split into short-range and long-range contributions.

Large-core pseudopotentials such as the LANL effective core potentials [182–184] can be placed on MM cations close to the QM region. These provide an accurate description of short-range QM-MM interactions, as they prevent spillage of electrons out of the QM region and also correct for the effect of the QM region termination on the one-electron states. Pseudopotentials are not usually used for anions as there is a general lack of available parameters. Moreover, anionic pseudopotentials are not supported in many molecular QM codes. However, this is not a serious issue as anions inherently repel electrons from the QM region and hence act as a natural electrostatic barrier to electron spillage.

The long-range contribution of the embedding potential is purely electrostatic and is typically handled by including the partial charges of the MM ions in the Hamiltonian during the QM calculation. This is equivalent to electrostatic embedding. The second term in the right hand side of Equation 3.85 represents the energy due to the effect of the embedding potential on the QM nuclei and is modelled classically using interatomic potentials.

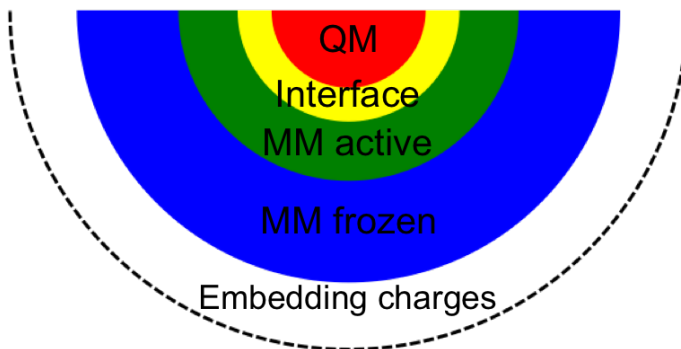


Figure 3.11: Schematic of the embedded cluster approach by Sokol *et al.*

The remaining two-body interactions (second term on the right hand side of Equation 3.84) are those between ions in the MM region. These are modelled classically using Coulombic and interatomic potentials. Under the assumption that the system is mostly ionic, it is normally sufficient to only consider two-body terms and neglect

higher-order many-body terms.

To include the long range electrostatic potential due to the bulk in the cluster system, a set of embedding charges are included on the exterior of the cluster. The embedding charges form a radial grid and are parameterised to minimise the error between the periodic and cluster electrostatic potential. The magnitudes of the embedding charges are parameterised using a least squares approach to minimise the error between the cluster and periodic electrostatic potential, calculated classically from atom-centred point charges with user specified magnitudes, for a set of grid points within the cluster. Also included in embedding charges are 2 point charges along each axis on opposite sides of the cluster and separated by a long distance. The magnitudes of these charges are analytically derived to reproduce the electrostatic dipole parallel to the corresponding axes.

3.5.4 Applications of the embedded cluster model

The embedded cluster QM/MM methodology by *Sokol et al.* has been employed in a variety of studies on ionic surfaces. French *et al.* employed the methodology in a study of the mechanisms associated with the catalytic conversion of CO₂ to methanol on the Cu/ZnO/Al₂O₃ catalysis [185]. They accurately reproduced the experimental desorption energy of CO from the polar (000 $\bar{1}$) ZnO surface and used this information along with the desorption energies of other species to obtain the reaction energies for the full catalytic cycle.

Bromley *et al.* studied interaction of neutral and charged Cu_{*n*} (*n* = 1-4) cluster with the polar ZnO (000 $\bar{1}$) surface [186]. Adsorption energies were computed and considered in conjunction with the likelihood of electron transfer to deduce mechanisms of surface cluster growth.

Goumans *et al.* studied the formation of water on interstellar dust grains on the forsterite (Mg₂SiO₄) (010) surface using the nudged elastic band method [187]. The calculated adsorption geometry and energy of water on the surface closely matched those predicted by periodic QM calculations. The deduced water formation mechanisms exhibited the catalytic nature of the surface.

Berger *et al.* studied the energetics of neutral and charged oxygen vacancies at the rutile TiO₂ (110) surface [188]. The density of states of the cluster system closely matched those of the periodic counterpart, thus validating the embedded cluster methodology.

Key technical details (cluster size, QM region and method etc.) of the QM/MM

embedded cluster methodology employed in the studies described above as well as those of other reported studies are summarised in Table 3.2. These are used as reference during testing of the methodology developed in Chapter 6.

System	Cluster size	QM atoms	Interface	Active region	Ref.
ZnO	~3000 atoms; 250 PCs	12	13 Zn PPs	~600 atoms	[185]
ZnO	4200 atoms ($r=25$); 125 PCs	13	33 Zn PPs	426 atoms ($r=13$)	[186]
ZnO	3000 atoms ($r=25$); 125 PCs	12-13	22 Zn PPs	~400 atoms ($r=13$)	[181]
ZnO	$r=25$	13-14	Zn PPs	No optimisation	[189]
Edingtonite	$r=25$	18	Link-atoms	Unknown	[190]
Mg ₂ SiO ₄	1684 atoms ($r=20$); 233 PCs	34	21 Mg ²⁺ PPs	164 atoms	[187]
MgO	6433 atoms ($r=30$)	22-29	Mg ²⁺ PPs	~3700 atoms ($r=25$)	[191]
TiO ₂	~3000 atoms ($r = 25$); 64 PCs	65-137	Ti PPs	QM atoms+MM shells	[188]

Table 3.2: Specifications of the clusters employed in a range of finite embedded cluster studies using the approach by Sokol *et al.* Radii (r) values are given in Angstrom. PC = point charge; PPs = pseudopotentials.

3.6 Geometry optimisation

The aim of geometry optimisation is to find minima in the potential energy surface to determine equilibrium geometries, which are stable states of the system being studied. Mathematically, a stationary point in the potential energy surface occurs when the first derivative of the potential energy with respect to each internal coordinate is zero. If each second derivative with respect to each internal coordinate at a stationary point is greater than zero, the stationary point is a minimum. For simple analytical functional forms, minima are readily found using standard calculus. However, as the potential energy surface is so complex - it has $3N-6$ degrees of freedom, where N is the number of atoms - the search for configurations that correspond to minima is not a trivial task.

There are many methods, commonly referred to as minimisation algorithms, that are currently used in geometry optimisation to search for such minima. In general, minimisation algorithms can be divided into those which use the energy derivatives and those which do not. The energy derivatives contain information of the shape of the energy surface and hence can be used to boost the efficiency of the minimisation algorithm. However, this comes at a cost of higher computational memory required to store the derivatives.

There is no undisputed best algorithm - the most suitable algorithm depends on the system being studied. For example, algorithms that use matrix inversion are more suited for smaller systems, and are therefore used more for QM calculations. Most algorithms only go downhill along energy surface and so cannot be used to locate multiple minima nor guarantee identification of the global minimum. In fact, no algorithm can guarantee the global minimum to be found. This is usually attempted by generating a wide range of starting configurations, each of which is then minimised. Calculation of energy derivatives can be performed analytically or numerically. The former is preferred as the calculations involved are quicker and exact. However, if analytical derivatives cannot be obtained, it may be better to use an algorithm that does not use energy derivatives. A few of the commonly used methods will be described in detail here.

Steepest descent

In the steepest descent minimisation algorithm, the configuration evolves in the direction parallel to the net force, equivalently the opposite direction to the gradient vector, $\mathbf{g}_k$. The procedure is then to search along that direction to find the closest minimum point, at which then the system will move along the direction parallel to the net force, always orthogonal to the previous direction. This process is iterated until the pre-

defined convergence criteria is reached. The steepest descent algorithm is a very simple algorithm that is easy to implement and only requires storage of a gradient vector. The downside is that the rate of convergence slows down as the minimum is approached. Furthermore, the minimum point can never be fully reached - the descent path instead ‘zig-zags’ close to the real minimum. This can be particularly problematic if the local energy surface around the minimum is characterised by long narrow ‘valleys’.

Conjugate gradient

The steepest descent algorithm can be inefficient as each step along a direction partially undoes the previous step. The conjugate gradient algorithm improves on the steepest descent algorithm by performing each line search along a direction that is a mixture of the current negative gradient and the previous search direction.

$$\mathbf{v}_k = -\mathbf{g}_k + \gamma_k \mathbf{v}_{k-1} , \quad (3.86)$$

where the constant γ_k is given by

$$\gamma_k = \frac{\mathbf{g}_k \cdot \mathbf{g}_k}{\mathbf{g}_{k-1} \cdot \mathbf{g}_{k-1}} . \quad (3.87)$$

As a previous direction is needed for the conjugate gradient algorithm, the steepest descent algorithm is usually used for the first step. The conjugate gradient algorithm works best for near quadratic surfaces, and can more efficiently achieve convergence. More storage is required to store the previous search direction as well as the gradient vector, though this is rarely a problem considering today’s computing power.

Newton-Raphson

Consider in one dimension the standard Taylor expansion of a function $f(x)$ about the point x_k expanded to second order:

$$f(x) \approx f(x_k) + (x - x_k)f'(x_k) + \frac{(x - x_k)^2}{2}f''(x_k) , \quad (3.88)$$

where $f'(x_k)$, $f''(x_k)$ are the first and second derivatives of $f(x)$ about x_k respectively. This can be generalised for a multi-dimensional energy function $f(\mathbf{x})$:

$$f(\mathbf{x}) \approx f(\mathbf{x}_k) + \mathbf{g}^t(\mathbf{x} - \mathbf{x}_k) + \frac{1}{2}(\mathbf{x} - \mathbf{x}_k)^t \mathbf{H}(\mathbf{x} - \mathbf{x}_k) , \quad (3.89)$$

where $\mathbf{g}$ is the gradient vector and $\mathbf{H}$ is the Hessian matrix containing the second derivatives. The superscript t denotes a transpose. Requiring the derivative of Eq. 3.89 to be zero leads to the Newton-Raphson step:

$$(\mathbf{x} - \mathbf{x}_k) = -\mathbf{H}^{-1} \mathbf{g}. \quad (3.90)$$

By performing the appropriate unitary transformation, a new coordinate system can be reached in which the Hessian is diagonal. In this new coordinate system, the Newton-Raphson step can be written as:

$$\delta \mathbf{x}' = (\delta x'_1, \delta x'_2, \dots, \delta x'_N), \quad (3.91)$$

where

$$\delta x'_i = -\frac{f_i}{\epsilon_i}. \quad (3.92)$$

Here, f_i is the projection of the gradient along the i th Hessian eigenvector with eigenvalue ϵ_i . The stationary point is not exactly reached from this step as the real energy function is an infinite series. Like the steepest descent and conjugate gradient algorithms, the Newton-Raphson method is therefore applied iteratively. If one or more of the Hessian eigenvalues are negative, the Newton-Raphson step will be in the same direction as, rather than opposite to, the gradient vector. In this case, the optimisation may reach a saddle point, or a maximum if all eigenvalues are negatives.

The Newton-Raphson algorithm is much faster than steepest descent. However, Newton-Raphson requires full calculation of the second derivative matrix, which must be stored and then inverted. This can be computationally demanding (can be an order of magnitude more demanding than calculating the gradient) if the system is large. To avoid this possible bottleneck, Quasi-Newton methods that instead approximate the Hessian using gradient evaluations have been developed. One such algorithm is the Broyden-Fletcher-Goldfarb-Shanno (BFGS) scheme, outlined below.

The Broyden-Fletcher-Goldfarb-Shanno (BFGS) scheme

Quasi-Newton minimisation algorithms avoid the computationally demanding step of calculating the Hessian matrix at each optimisation step. The initial Hessian matrix is approximated using for example a unit matrix, or a Hessian calculated at a lower level of theory. At each subsequent iteration of the optimisation procedure, the gradients at the current point is used to update the Hessian so that it provides a better approximation of the exact Hessian. There are many updating schemes such as Davidon-Fletcher-

Powell (DFP) [192, 193], Powell [194], and Broyden-Fletcher-Goldfarb-Shanno (BFGS) [195–198]. For geometry optimisation, the Broyden-Fletcher-Goldfarb-Shanno (BFGS) scheme is normally used as it ensures that the Hessian is positive definitive, which ensures a minimum point is reached. In the BFGS scheme, the Hessian is updated each optimisation step as follows:

$$\mathbf{H}_n = \mathbf{H}_{n-1} + \Delta\mathbf{H}, \quad (3.93)$$

where

$$\Delta\mathbf{H} = \frac{\Delta\mathbf{g}\Delta\mathbf{g}^t}{\Delta\mathbf{g}^t\Delta\mathbf{x}} - \frac{\mathbf{H}\Delta\mathbf{x}\Delta\mathbf{x}^t\mathbf{H}}{\Delta\mathbf{x}^t\mathbf{H}\Delta\mathbf{x}}. \quad (3.94)$$

As the Hessian is approximated, it is clear that the BFGS algorithm will not achieve convergence as fast as Newton-Raphson methods in terms of the number of iterations. However, as direct computation of the Hessian is avoided, the overall computational effort may be less. The BFGS algorithm is employed in all geometry optimisations performed in this work.

3.7 Conclusions

In this chapter, a host of theoretical methods and techniques relevant to this work have been introduced. First, the theory and capabilities of various total energy methods, including classical MM, QM electronic structure methods (HF and DFT), and hybrid QM/MM, were given. It is clear that a pure MM approach is unsuited to achieve the aims of this work due to the combination of the lack of high quality parameters specific to the CuFeS₂ system and the inability to model the electronic structure, which is vital to understand charge transfer and chemical mechanisms. In the study of the bulk properties (Chapter 4) and surface morphology (Chapter 5) of CuFeS₂, periodic DFT with the hybrid exchange functional B3LYP, which has shown to be reliable for a range of strongly correlated materials, is employed.

Some of the technical details relevant to the modelling of surfaces were described in this chapter. Tasker’s classifications of ionic surfaces, which is a useful tool to quickly identify potentially stable surfaces, is employed in Chapter 5. The slab and cluster models to represent surfaces, which are used in Chapter 5 and 6 respectively, were introduced.

Several finite cluster methods used to model systems with localised features, such as a bulk crystal with a point defect, were also introduced in this chapter. The advantage of these methods over the simpler periodic approach is the avoidance of artificial

periodic interactions such as defect-defect interactions. In particular, the theory and applications of the QM/MM embedded finite cluster method by Sokol *et al.*, which was developed specifically for modelling defects on ionic surfaces, has been described. Their approach has been chosen as the basis for the development and testing of a hybrid QM/MM cluster methodology for the CuFeS₂ system (Chapter 6).

4

Bulk CuFeS₂

4.1 Introduction

In order to study the surface chemistry of CuFeS₂, it is vital to have thorough understanding of the fundamental properties of bulk CuFeS₂. It was concluded from the review of previous studies conducted on bulk CuFeS₂ (Section 2.2) that the crystal structure is well established but there is still some uncertainty with regards to the electronic properties, particularly in the value of the band gap. On the experimental side, it has been acknowledged that some of the uncertainty could be due to impurities in the crystal sample, or pressure induced lattice modifications [62]. Theoretically, there have been a number of published studies employing density functional theory (DFT).

However, most of these have employed either the local density approximation (LDA) or the generalised gradient approximation (GGA) for exchange and correlation and predict CuFeS₂ to be either conducting [62], or with a small band gap that is much lower than reported experimental values [54, 55]. It is apparent that the electronic structure and physical properties of CuFeS₂ are sensitive to the correct treatment of on-site electronic interactions for which the LDA and GGA are not reliable approximations [64]. In the current work, the hybrid-exchange Becke three parameter (exchange), Lee-Yang-Parr (correlation) functional (B3LYP) functional is employed as compared to LDA and GGA, it provides a more accurate description of the electronic structure of localised and strongly interacting systems that are non-conducting due to partial correction of electronic self-interaction.

Recently, Conejeros *et al.* performed a B3LYP investigation of bulk CuFeS₂, although the study focused more on the magnetic behaviour of CuFeS₂ at low temperatures, rather than the electronic structure [63]. In particular, they concluded that

copper atoms behave diamagnetically in the range 170-300 K and that this was not due to partial oxidation but because of magnetic excitations on Fe spins which increase the amount of spin delocalisation on neighbouring CuS₄ tetrahedra.

The purpose of the study of bulk CuFeS₂ presented here is twofold. First, is the validation of the adopted B3LYP methodology through comparison of calculated properties, such as lattice parameters, to well established experimental and theoretical values. Second, is to provide clarification of the electronic properties. This includes the value of band gap as well as the reason for the lower than expected magnetic moment of Fe. To achieve this, a thorough analysis of the electronic structure and the nature of the bonding in CuFeS₂ is conducted. In particular, the Hubbard-Anderson model is used to rationalise the electronic structure and the nature of the Cu-S and Fe-S bonds through comparison with related materials. This chapter is organised as follows: Section 4.2 describes the computational method deployed. In Section 4.3 the geometry and electronic structure of the CuFeS₂ bulk ground state are presented and discussed along with a comparison with Cu₂S and Fe₃S₄. Finally, the main conclusions of this study are summarised in Section 4.4.

The work presented in this chapter has been published as R. Martínez-Casado, V. H.-Y. Chen, G. Mallia and N. M. Harrison, *J. Chem. Phys.*, **144**, 184702, 2016. Dr. Martínez-Casado performed the initial calculations to test the basis sets and validate the methodology. I performed the final calculations used to generate the data presented in the article and conducted detailed analysis of the density of states to determine the electronic structure and bonding properties of CuFeS₂. In addition, I wrote the final version of the manuscript. Guidance was provided by Dr. Mallia and Prof. Harrison for this work.

4.2 Computational details

All calculations have been performed using the CRYSTAL09 software package [199,200], based on the expansion of the crystalline orbitals as a linear combination of a local basis set (BS) consisting of atom centred Gaussian orbitals. The BSs used for this work are all-electron BSs based on pre-existing ones from the literature. The BS for Cu was optimised by Doll and Harrison and used for their study of chlorine adsorption on the Cu(111) surface [201]. It consists of an 86-4111 d (41) contraction [one s , five sp , and two d shell(s)]; the most diffuse $sp(d)$ exponents are $\alpha_{\text{Cu}}=0.150(0.392)$ Bohr⁻². The BS for Fe was based on the one employed by Catti *et al.* for their study of α -Fe₂O₃ (hematite) [202]. This BS has been adapted for this work by adding an additional

diffuse sp shell consisting of a single Gaussian basis function with an appropriately chosen exponent so that the number of valence shells matches that of the Cu BS. The resulting BS, like the Cu BS, consists of an 86-4111 $d(41)$ contraction [one s , five sp , and two d shell(s)]; the most diffuse $sp(d)$ exponents are $\alpha_{\text{Fe}}=0.225(0.4345)$ Bohr $^{-2}$. The BS for S was optimised by Azavant and Lichanot and used for their study of Li₂S [203]. It consists of an 86-311 $d(1)$ contraction [one s , four sp , and one d shell(s)]; the most diffuse $sp(d)$ exponents are $\alpha_{\text{S}}=0.106(0.383)$ Bohr $^{-2}$. The exponents and coefficients of the basis sets are given in Appendix A.

Electronic exchange and correlation are approximated using the hybrid-exchange B3LYP functional [135, 137], which has previously shown to provide a reliable ground state description of geometric parameters, band structures, and electronic and magnetic properties in a range of strongly correlated (mainly transition metal oxides) materials [204–211]. It has also been reported that the B3LYP functional reproduces the band gap of a wide range of materials including, semiconductors, sulfides and semi-ionic, ionic and transition metal oxides [64, 212, 213].

Matrix elements of the exchange and correlation potentials and the energy functional are integrated numerically on an atom-centred grid of points. The integration over radial and angular coordinates is performed using Gauss-Legendre and Lebedev schemes, respectively. A pruned grid consisting of 99 radial points and 5 sub-intervals with (146, 302, 590, 1454, 590) angular points has been used for all calculations (the XXLGRID option implemented in CRYSTAL09 [199, 200]). This grid converges the integrated charge density to an accuracy of about $\times 10^{-6}$ electrons per unit cell. The Coulomb and exchange series are summed directly and truncated using overlap criteria with thresholds of 10^{-7} , 10^{-7} , 10^{-7} , 10^{-7} and 10^{-14} as described previously [200, 214]. Reciprocal space sampling was performed on a Pack-Monkhorst net with a shrinking factor comparable to IS=4, which defines 14 symmetry unique k-points. The self consistent field procedure was converged up to a tolerance in the total energy of $\Delta E = 1 \cdot 10^{-7} E_h$ per unit cell.

The cell parameters and the internal coordinates have been determined by minimisation of the total energy within an iterative procedure based on the total energy gradient calculated analytically with respect to the cell parameters and nuclear coordinates. Structural optimisation was performed using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) scheme, as implemented in CRYSTAL09 [199, 200]. Convergence was determined from the root-mean-square (rms) and the absolute value of the largest component of the forces and displacements. The thresholds for the maximum and the rms forces (the maximum and the rms atomic displacements) have been set to 0.00045 and 0.00030

(0.00180 and 0.00120) in atomic units. Geometry optimization was terminated when all four conditions were satisfied simultaneously. Ionic charges were determined using a Mulliken partition of the total charge density, as implemented in CRYSTAL09 [199, 200].

In order to gain further insight into the nature of bonding in CuFeS₂ and verify the Cu⁺Fe³⁺(S²⁻)₂ oxidation state, the geometric and electronic structure of CuFeS₂ has been compared with that of chalcocite (Cu₂S) and greigite (Fe₃S₄), chosen as from a formal charge point of view they contain ions in the same oxidation states, partially in the case of Fe₃S₄. For chalcocite, the monoclinic “low chalcocite” phase was considered in this work as this is the most stable phase under standard atmospheric conditions. The oxidation state of Cu₂S has been established as (Cu⁺)₂S²⁻, from the analysis of near-edge X-ray adsorption fine structure (NEXAFS) spectra obtained by Goh *et al.* [215]. Greigite, which has a spinel structure and a cubic unit cell, is believed to form from the oxidation of two thirds of Fe²⁺ cations in mackinawite (Fe²⁺S²⁻), in addition to rearrangement of the cubic S anion sublattice [216]. Greigite has two types of Fe sites; in each unit cell there are 8 tetrahedrally coordinated ferric (Fe³⁺) cations (type A sites) and 16 octahedrally coordinated Fe that are a mixture of ferric (Fe³⁺) and ferrous (Fe²⁺) cations (type B sites) [217]. The structures of Cu₂S and Fe₃S₄ were optimised using the same numerical procedures and basis sets described above.

4.3 Results

4.3.1 Geometry

Chalcopyrite (CuFeS₂) has a tetragonal unit cell of $\bar{4}2d$ symmetry containing two Cu, two Fe and four S atoms. Optimising the structure of CuFeS₂ by varying the cell and all internal coordinates while imposing $\bar{4}2d$ symmetry results in the structure documented in Table 4.1 and visualised in Figure 4.1. Table 4.1 also includes lattice constants and bond lengths determined from previous DFT studies using various approximations for the electronic exchange and correlation including LDA [54] and GGA [3, 54]. The table also presents experimental lattice constants deduced from X-ray diffraction on a natural single crystal specimens by Kratz *et al.* [50].

The tendency of LDA to overbind is well documented [213], however the underestimation of the lattice parameters by 5-6% reported by Zhou *et al.* [54] is significantly greater than what is typically observed for insulators (~1-2%). The lattice parameters estimated using the GGA functionals PBE and PW91, by Zhou *et al.* [54] and Łazewski *et al.* [3] respectively, provide a significant improvement on the estimated lattice con-

stants. In the case of the latter, the estimated lattice parameters are unexpectedly close to the experimental ones. The general trend that GGA functionals tend to overcorrect the overbinding by LDA leading to the overestimation of lattice parameters for ionic insulators does not hold here [141, 213, 218]. For this work, the optimised lattice parameters differ slightly from experiment, with **a** and **c** overestimated by 3%. The discrepancy with experiment is due more to the overestimation of the Cu-S bond length ($\sim 4\%$) rather than the Fe-S bond length ($\sim 2\%$). The slight overestimation of lattice parameters and bond lengths is typical for ionic insulators when using the B3LYP functional [141, 213]. This may in part be due to the neglect of London dispersion interactions.

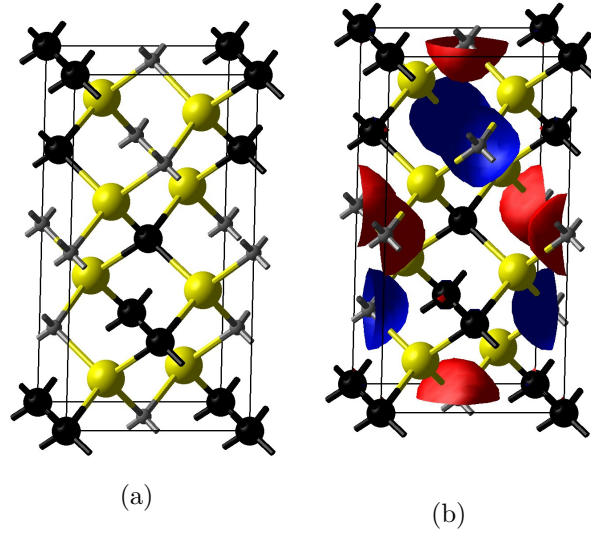


Figure 4.1: On the left (a) the crystallographic cell for CuFeS_2 showing the optimised geometry described in Table 4.1. Large (yellow), medium (black) and small (silver) spheres correspond to S, Cu and Fe atoms respectively. In the right (b) the same cell is shown with the spin density isosurfaces drawn at -0.005 (blue) and $+0.005$ (red) $|\mu_B|/\text{Bohr}^3$. This illustrates the antiferromagnetic nature of the Fe spins.

4.3.2 Electronic structure

In this section the electronic structure of CuFeS_2 is analysed in terms of charges from Mulliken population analysis q , Born effective charges Z^* , the spin density and moments μ_B , the total and projected density of states and the band gap. The population analysis suggests ionic charges of $q_{\text{Cu}} = +0.483|e|$, $q_{\text{Fe}} = +1.393|e|$, and $q_{\text{S}} = -0.938|e|$, implying a semi-ionic model of bonding in CuFeS_2 . However, charges obtained from Mulliken

Param.	Expt.	LDA	GGA-PBE	GGA-PW91	Current work
a	5.286	4.955 (-6.3)	5.080 (-3.9)	5.265 (-0.4)	5.452 (3.1)
c	10.410	9.851 (-5.4)	10.003 (-3.9)	10.534 (1.2)	10.710 (2.9)
$d_{\text{Cu-S}}$	2.299			2.305 (0.3)	2.395 (4.2)
$d_{\text{Fe-S}}$	2.256			2.256 (0.0)	2.301 (2.0)
Ref.	[50]	[54]	[54]	[3]	

Table 4.1: Optimised geometry for CuFeS₂ and comparison with previous theoretical results and experimental values obtained using X-ray diffraction. All quantities are in units of Angstroms. The percentage error of lattice constants and bond lengths relative to experiment are given in parentheses.

population analysis are dependent on the choice of local basis set and so do not provide a definitive picture of the bonding. In Table 4.2 the Born effective charge tensors of Cu, Fe and S which were computed using the Berry phase method are shown [219]. The Born effective charges of Cu, Fe, and S, which correspond to 1/3 of the respective charge tensors are $Z_{\text{Cu}}^* = 0.95$, $Z_{\text{Fe}}^* = 2.96$ and $Z_{\text{S}}^* = -1.97|e|$. These charges support a rather ionic model of the electronic structure of CuFeS₂ as $\text{Cu}^+\text{Fe}^{3+}(\text{S}^{2-})_2$. The Born charges computed from GGA-PW91 calculations by Lazewski *et al.* [3] ($Z_{\text{Cu}}^* = 0.75$, $Z_{\text{Fe}}^* = 3.55$, and $Z_{\text{S}}^* = -2.15$) portray a slightly different picture of bonding in which the degree of covalency is higher. This suggests that the on-site Coulomb repulsion, which is more accurately modelled by the B3LYP functional, plays an important role in the bonding. The Born effective charges are not consistent with an ionic model based on $\text{Cu}^{2+}\text{Fe}^{2+}(\text{S}^{2-})_2$ which, as mentioned in Section 4.1, has been proposed as an explanation for the lower than expected magnetic moment of Fe [48, 220].

Model	Z_{Cu}			Z_{Fe}			Z_{S}		
B3LYP	1.04	-0.04	0.0	2.81	-0.25	0.0	-1.76	0.0	0.0
	-0.04	1.04	0.0	0.25	2.81	0.0	0.0	-2.11	1.12
	0.0	0.0	0.76	0.0	0.0	3.27	0.0	1.03	-2.03
GGA [3]	0.90	0.17	0.0	3.43	-0.21	0.0	-2.12	0.0	0.0
	-0.17	0.90	0.0	0.21	3.43	0.0	0.0	-2.20	1.08
	0.0	0.0	0.46	0.0	0.0	3.80	0.0	1.53	-2.13

Table 4.2: Comparison of the calculated DFT-B3LYP Born effective charges tensors with those obtained in previous works based on GGA-PW91 calculations by Lazewski *et al.* [3].

In the ground state antiferromagnetic solution, the calculated spin moment of the two Fe atoms in the unit cell are +3.93 and -3.93 μ_{B} . This magnetic configuration is

visualised via a plot in which isosurfaces of the spin density is overlayed on top of the optimised unit cell, shown in Figure 4.1b. This confirms that CuFeS₂ is antiferromagnetic with spin moments aligned within atomic layers parallel to the crystallographic a, b plane and opposing along the crystallographic c direction.

The antiferromagnetic state is found to be 0.303 eV per formula unit lower in energy than the fully ferromagnetically coupled state. This is compared with the antiferromagnetic-ferromagnetic coupling of 0.445 eV per formula unit calculated by Conejeros *et al.*, who also used the hybrid-exchange B3LYP functional [63]. The discrepancy may be attributable to the different basis sets used in their calculations.

The results presented here are consistent with both experiment and previous theoretical studies. The calculated (absolute) Fe spin moments of $3.93 \mu_B$ are close to the values of $3.85 \mu_B$ deduced from neutron diffraction measurements by Donnay *et al.* [51] and $3.89 \mu_B$ from DFT-B3LYP calculations by Conejeros *et al.* [63]. The calculated spin moments is less than the value expected for an Fe³⁺ ion ($5 \mu_B$) but it can nevertheless be concluded from examination of the population analysis of individual orbitals that each Fe d -orbital is singly-occupied, which provide support to the Fe³⁺ ($3d^5$) oxidation state. The tetrahedral crystal field results in an unpaired electron occupying each of the two energetically lower e -symmetry states (the spin moment for each orbital is $\sim 0.86 \mu_B$) and an unpaired electron occupying each of the three energetically higher t_2 -symmetry states (the spin moment for each orbital is $\sim 0.70 \mu_B$). The slight reduction of the spin from $1 \mu_B$ in each orbital is due to hybridization of $3d$ -Fe with $2p$ -S. No spin is localised on the Cu and S, which again is consistent with the Cu⁺Fe³⁺(S⁻²)₂ oxidation state.

The density of states (DOS) (total and that projected onto Cu, Fe and S) of the optimised ground state of CuFeS₂ are plotted in Figure 4.2. For Fe, the DOS are further projected onto the two individual Fe atoms of the unit cell, labelled “spin-up” and “spin-down” sites. In addition, the DOS contributions from spin-up (α) electrons and spin-down (β) electrons are plotted separately, above (in solid) and below (in dashed) the x -axis respectively. This allows the antiferromagnetic nature of the CuFeS₂ ground state to be clearly seen. Centred around an energy of -6.5 eV below the valence band maximum (VBM), there is a highly localised band of $3d$ -Fe states which indicate that the Fe-S interactions are strongly ionic. However, these states are somewhat hybridised with $3p$ -S states which, as mentioned before, explains the lower magnetic moment compared to what is expected for a purely ionic system. Compared to Fe, the contributions of the valence Cu $3d$ -states are spread over several bands between around -5.4 eV and the VBM. The dispersion of the $3d$ -Cu states is attributed to

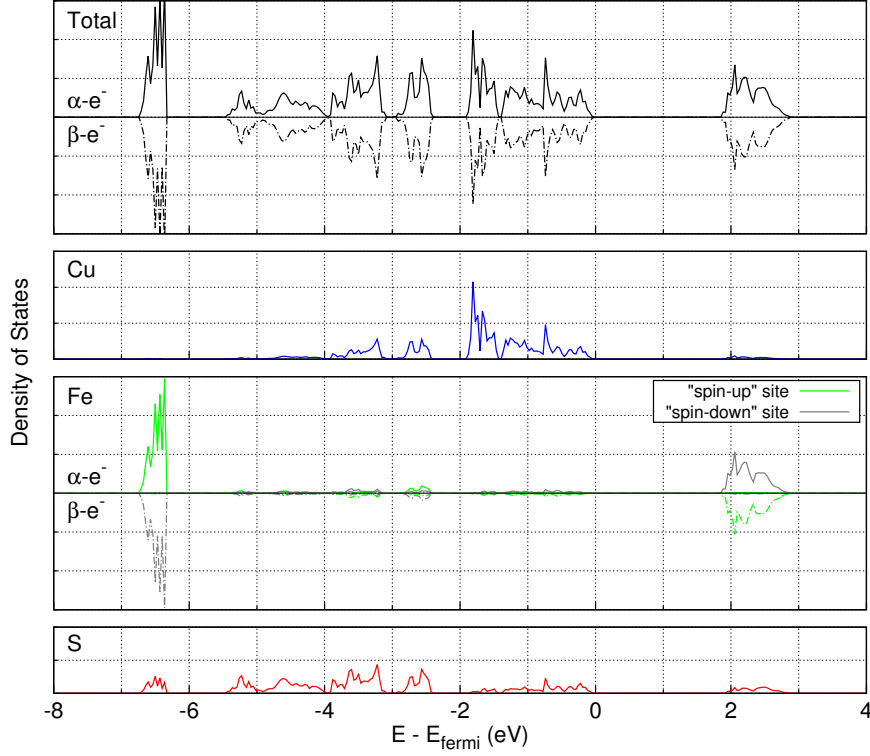


Figure 4.2: Density of states (DOS) for the antiferromagnetic ground state solution of CuFeS_2 . The DOS are also projected onto Cu, Fe and S. For Fe, the DOS are split into contributions from spin-up (α) and spin-down (β) electrons and further projected onto the two individual Fe atoms of the unit cell - labelled “spin-up” and “spin-down” site. In all subfigures each tick on the y -axis represents 250 States/Energy/Cell.

covalent interactions with $3p$ -S states, apparent in the large degree of overlap of $3d$ -Cu and $3p$ -S states in the energy range. More evidence of covalent Cu-S interactions can be observed by separating the $3d$ -Cu states further into those attributed to t_2 or e orbitals, as seen in Figure 4.3. The plot shows that the dispersion of the $3d$ -Cu states is mostly due to the spread in the energy levels of the t_2 states, whose corresponding orbitals are pointed in the direction of Cu-S bonds. In summary, analysis of the DOS suggests that the electronic structure of CuFeS_2 may be described in a semi-ionic model with localised, ionic, Fe- d -electrons and more covalent Cu- d -S- $2p$ interactions.

The B3LYP band gap estimated from the eigenvalues is 1.82 eV and in disagreement with previous theoretical studies using different treatments of electronic exchange and correlation. LDA calculations performed by Edelbro *et al.* predicted CuFeS_2 to be conducting [62] while GGA-PW91 calculations performed by de Oliveira *et al.* predicted

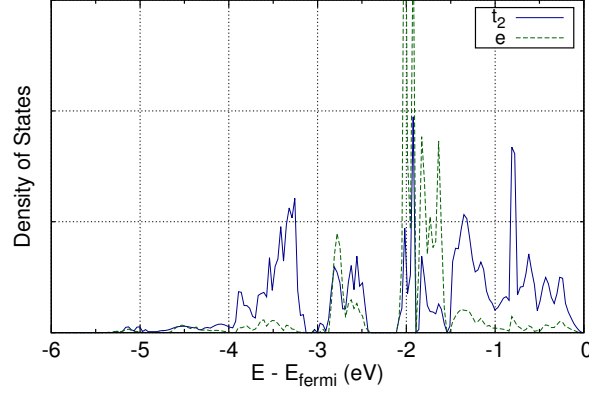


Figure 4.3: Density of states (DOS) for CuFeS_2 projected onto Cu and split into contributions from t_2 and e orbitals.

CuFeS_2 to be a semiconductor with an indirect band gap of 0.1 eV [55]. The estimated band gap here is identical to the B3LYP band gap calculated by Conejeros *et al.* [63]. There is no clear consensus on the measured band gap as discussed in Section 4.1; band gaps of between 0.33-2.6 eV have been reported [58, 59, 65]. As mentioned in Sec 4.2, the B3LYP functional is generally more reliable for estimating the electronic band gap than LDA or GGA, which tend to underestimate the band gap [64].

4.3.3 Comparison with Cu_2S and Fe_3S_4

The projected DOS of Cu_2S (top), CuFeS_2 (middle), and Fe_3S_4 (bottom) are plotted separately in Figure 4.4. For ease of comparison, the CuFeS_2 DOS are only projected on one (the “spin-up” site) of the two Fe sites in the unit cell. For Fe_3S_4 , the 3d-Fe DOS are separated into states belonging to type A Fe or type B Fe sites, as described in Section 4.2. This allows Fe-S interactions in CuFeS_2 and Fe_3S_4 to be compared for Fe of identical oxidation state (Fe^{3+}) and coordination (tetrahedral).

Despite Cu and S being in the same oxidation state (Cu^+ ; S^{2-}) in both Cu_2S and CuFeS_2 , the bonding structure of the two compounds is rather different. The optimised crystal structure of Cu_2S is complex; Cu atoms are mostly in triangular coordination with S with Cu-S bonds that vary in length from 2.24 to 2.69 Å with an average length (2.39 Å) similar to the length of Cu-S bonds in CuFeS_2 (2.40 Å). In addition, Cu_2S has a more tightly packed crystal structure; each Cu atom is also closely neighbored (separation of between 2.5 and 3.0 Å) to several (between 2 and 5) other Cu atoms while most S atoms are six-fold coordinated to Cu. In the DOS of Cu_2S two valence

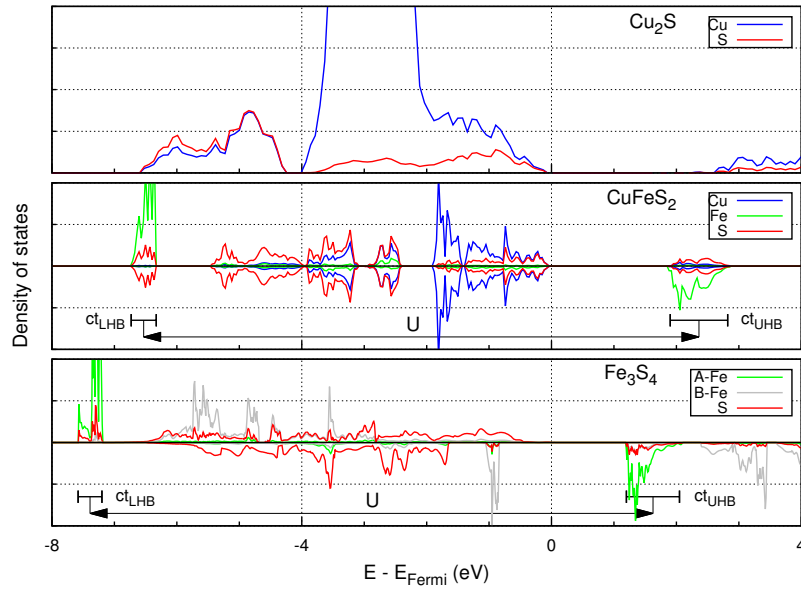


Figure 4.4: Projected density of states for CuFeS_2 , Cu_2S and Fe_3S_4 . For CuFeS_2 (mid) and Fe_3S_4 , the spin up (α) and spin down (β) electrons are plotted above and below the y -axis respectively.

bands can be identified about the Fermi energy. The upper band between -4.0 eV and the VBM consists of mostly $3d$ -Cu states weakly mixed with $3p$ -S states while the lower band between -6.5 and -4.2 eV consists of a roughly equal mixture of $3d$ -Cu and $3p$ -S states. The strong hybridization in the lower valence band suggests that Cu_2S is a semi-ionic compound. As the electronic structure is based on a fully occupied Cu d -band the effects of the on-site Coulomb repulsion are not visible. The overall width of the combined valence $3p$ -S and $3d$ -Cu bands (~ 6.6 eV) in Cu_2S exceeds that of its counterpart in CuFeS_2 (~ 5.5 eV), which is expected since there is more overlap of valence orbitals in Cu_2S due to its greater Cu-S coordination and shorter bond lengths. Considered in conjunction with the strong hybridization of $3p$ -S and $3d$ -Cu states in the lower valence band this suggests that the degree of covalency of Cu-S bonds is higher in Cu_2S than in CuFeS_2 . In summary, Cu-S interactions in Cu_2S and CuFeS_2 are similar in the sense that they have a mixed ionic and covalent character despite the different geometric coordination, and the degree of covalency is higher in Cu_2S .

The local structure of type A Fe sites in Fe_3S_4 is similar to that of Fe in CuFeS_2 . In addition to the Fe in both having tetrahedral coordination, the average type A Fe-S bond length of 2.33 Å is only slightly longer than the average Fe-S bond length in CuFeS_2 (2.30 Å). The splitting of the occupied and unoccupied Fe- d -states is due to strong on-site electron correlation. This is typically well described in the B3LYP approximation [205, 206, 221–223]. The electronic interactions in Fe_3S_4 can be mapped to that of a Hubbard-Anderson Hamiltonian of the form [224–226]:

$$H = \sum_i \epsilon_i n_{i\sigma} - t \sum_{\langle i,j \rangle \sigma} c_{i\sigma}^\dagger c_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow} \quad (4.1)$$

where ϵ_i is the energy of an Fe d -orbital, $c_{i\sigma}^\dagger$ and $c_{j\sigma}$ are annihilation and creation operators for d electrons of spin σ on Fe lattice sites i and j respectively, U represents the intra- d -electron Coulomb repulsion energy, t is the hopping integral representing the kinetic energy of electrons hopping between atoms, and n_i is the number operator for the site i . In the strong correlation regime ($U \gg t$) this produces an (occupied) lower and (unoccupied) upper Hubbard band, separated by an energy U . The Hubbard bands are of width ct where c is a constant that depends on the bonding environment of the Fe atoms. For example, c has a value of 2 for a 1D chain of atoms. As described previously, the bonding environment of the Fe sites of CuFeS_2 and A Fe sites of Fe_3S_4 are very similar. The c value for these two types of Fe sites are therefore expected to be very similar and hence it is not necessary to know the value of c here for the purpose of comparing the electronic structures.

Examining Figure 4.4, the lower and upper bands for the tetrahedrally coordinated type A Fe³⁺ site (marked ct_{LHB} and ct_{UHB}) are centred at -7.39 and 1.63 eV with widths of 0.38 and 0.85 eV, respectively. This suggests that the electronic structure may be modelled with a U value of 9.02 eV and ct value of 0.62 eV (average of ct_{LHB} and ct_{UHB}).

For CuFeS₂, the lower and upper Hubbard bands for 3d-Fe can be identified centred at around -6.53 and +2.36 eV respectively, implying a U value of 8.89 eV. Their respective bandwidths are 0.40 and 0.92 eV, giving an effective ct value of 0.66 eV. The parameters derived for Fe₃S₄ thus describe the electronic structure of CuFeS₂ rather well. The following can therefore be concluded: (1) Further confirmation that Fe in CuFeS₂ is in the Fe³⁺ oxidation state is obtained which in turn validates the Cu⁺Fe³⁺(S²⁻)₂ oxidation state. (2) The nature of Fe-S bonding in CuFeS₂ and Fe₃S₄ (for type A Fe) is very similar and essentially ionic. (3) In both cases the electrons of the Fe³⁺ site are highly localised and strongly correlated, corresponding to the $U \gg t$ regime in the Hubbard-Anderson model. It should be noted that the Hubbard U values deduced here are only indirectly related to that of the widely used DFT+ U approaches. In the GGA+ U approach employed for bulk CuFeS₂ by Zhou *et al.* [54], they determined an optimal U parameter of 3 eV, which is significantly different to the one determined here from the DOS.

4.4 Conclusions

In this chapter, a hybrid-exchange density functional study of the geometry and electronic structure of states of bulk CuFeS₂ has been presented. The calculated optimised structure of the chalcopyrite has lattice parameters and bond lengths in agreement with those measured with a slight overestimation of around 3%. The ground state of CuFeS₂ is found to be antiferromagnetic, agreeing with previous calculations and experiments. Analysis of the electronic structure through the projected density of states and spin moments reveals a mixed picture of bonding where the Fe³⁺ sites are strongly ionic while Cu⁺ sites are semi-ionic and engage in covalent interactions with S²⁻ ligands. The slight hybridization of 3d-Fe and 3p-S states accounts for the lower than expected spin density of the d^5 Fe³⁺. The calculated band gap of 1.8 eV is within the range of published experimental values and is likely to be more accurate than previous calculations using LDA or GGA functionals due to the use of the hybrid-exchange B3LYP functional, in the current study.

In comparison with Cu₂S, which adopts a significantly different bonding structure

compared with CuFeS_2 , it was found that Cu-S interactions in both materials are semi-ionic but with a higher degree of covalency in Cu_2S . Conversely, the properties of type A Fe^{3+} sites in Fe_3S_4 was found to close match that of CuFeS_2 Fe^{3+} sites, both in terms of the local geometry and electronic structure. For the latter, remarkably similar on-site repulsion ($U \sim 8.9$ eV) and hopping integral ($t \sim 0.3$ eV) values were deduced for CuFeS_2 and Fe_3S_4 when their $3d$ -Fe states were mapped to the Hubbard-Anderson model. It can be concluded from analysis of the electronic structure and spin density in addition to the comparison with Cu_2 and Fe_3S_4 that CuFeS_2 is best modelled using the oxidation state $\text{Cu}^+\text{Fe}^{3+}(\text{S}^{2-})_2$ and that both strong electronic correlation and covalent interactions play an important role in the bonding.

Through comparison with available experimental data, the B3LYP methodology adopted has been validated and shown to be robust for the CuFeS_2 system. The next chapter builds on this study of bulk CuFeS_2 and presents an investigation of surface properties and morphology of CuFeS_2 using the same B3LYP methodology.

5

Surface Morphology of CuFeS₂

5.1 Introduction

In Chapter 4, a B3LYP study of bulk CuFeS₂ was presented. With the ground state structure and properties now well established, a foundation has been provided for study of surface properties and morphologies. Previously in Section 2.3 it was discussed that experimental studies of CuFeS₂ surfaces thus far have only been able to determine elemental composition but not details of the surface morphology. It has consequently not been possible to establish the structure and composition of crystallite surfaces or to determine which facets are typically exposed in small crystallites. This is mainly due to the fact that CuFeS₂ exhibits poor cleavage, which means that any fracture will result in a variety of surfaces being exposed [84, 227]. Building upon the study of bulk CuFeS₂ in Chapter 4, the aim of this chapter is to establish realistic models of the surface structure, formation energies and crystallite morphology through *ab initio* calculations. This enables surfaces most likely to be exposed upon fracture to be identified hence providing candidate surfaces for further study of surface chemistry and dissolution mechanisms.

To ensure a manageable number of surfaces is considered for study at the *ab initio* level, the investigation is limited to low index surfaces and those deduced to be nonpolar according to Tasker's classifications [112]. Due to only a few number of published studies on theoretical investigations of CuFeS₂ surfaces, the particular surface orientations considered in this work is also influenced by previous studies (summarised previously in Section 2.3) of the surfaces of Cu(In,Ga)(S,Se)₂ (CIGS) compounds as the CIGS compounds share the same valence state and crystal structure as CuFeS₂. In particular, the polar (112)/($\overline{112}$) surface pair, which has been shown to be remarkably

stable both experimentally and theoretically for CIGS is considered here.

The rest of this chapter is organised as follows. Section 5.2 details the process used to identify possible stable low index surfaces as well as the methods used Section 5.3 discusses the results of the calculations, including geometric, electronic and thermodynamic properties of the surfaces leading to prediction of the surface morphology. Finally, Section 5.4 provides a summary of the chapter.

The work presented in this chapter has been published as V. H.-Y. Chen, G. Mallia, R. Martínez-Casado and N. M. Harrison, *Phys. Rev. B*, **92**, 155426, 2015.

5.2 Method

A systematic approach was employed to screen the surfaces investigated down to a manageable number for study at the *ab initio* level. It is important to note that the surfaces in this investigation are modeled using slabs where both terminations are relaxed simultaneously. Depending on the cleavage plane, the resulting slab may be asymmetric, which means the two surfaces of the slab are different. Such slabs are denoted using the term ‘surface pair’.

Initially, all stoichiometric slabs generated from cleaving the bulk crystal along planes with small Miller indices ($h, k, l \leq 3$) were considered. Using the ionic model with the formal charges of CuFeS₂ (+1, +3 and -2 for Cu, Fe and S respectively), the electrostatic dipole perpendicular to the surface for each of these slabs was calculated to classify the surfaces and surface pairs into non-polar or polar types. All polar slabs were filtered out, leaving a list of non-polar slabs which were then ranked in ascending order of bonds broken as a result of cleaving the bulk scaled by surface unit area. The top 10 slabs of the ranked list, representing surfaces or surface pairs with relatively few under-coordinated surface atoms, were further considered. These are the (212)/(212), (213)/(213), (322)/(322), (323)/(323), (223)/(223), (102), (110), (313)/(313), (111)/(111) and (221)/(221) surfaces and surface pairs whose respective Tasker classifications are types 2, 2, 2, 2, 2, 1, 1, 2, 2 and 2.

The geometry of these 10 slabs were further inspected and slabs with surface geometric features that are likely to be chemically unstable were eliminated from the investigation. As an example, the (111)/(111) surface pair shown in Fig. 5.1, was eliminated as it has one singly-coordinated S atom on the (111) surface per unit cell. Indeed, a test DFT calculation performed on the (111)/(111) slab resulted in failed convergence of the wavefunction during the self-consistent field (SCF) procedure. The remaining slabs, representing the (110) and (102) surfaces, both Tasker type 1, were

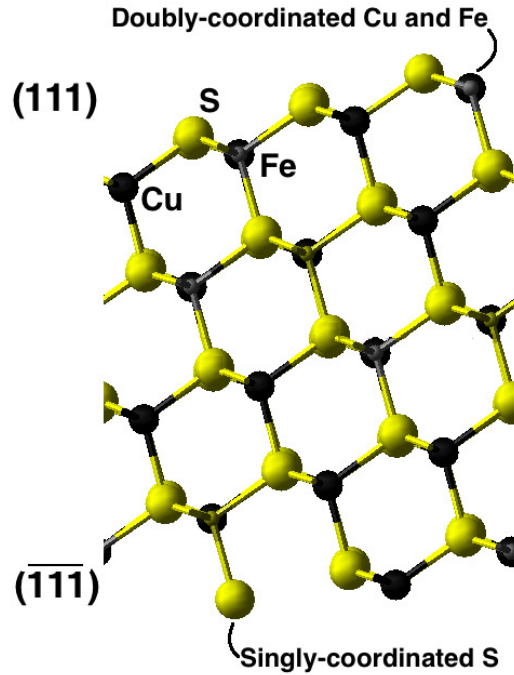


Figure 5.1: The unrelaxed non-polar $(111)/(\bar{1}\bar{1}\bar{1})$ slab. Copper, iron and sulphur atoms are coloured black, silver and yellow respectively. The most under-coordinated atoms are labelled.

investigated in this work. In addition, the non-polar (114) surface, also a Tasker type 1 surface, was investigated as it was reported to be stable from DFT-GGA calculation performed by de Oliveira *et al.* [85]. It may be possible that slabs eliminated during the filtering process can be stable in larger periodicities through the formation of complex reconstruction patterns. However this is beyond the scope of this investigation which is limited to the consideration (1×1) surface unit cells.

In addition to the non-polar surfaces, the polar cation-terminated (112) and anion-terminated $(\bar{1}\bar{1}\bar{2})$ (referred to as $(112)/(\bar{1}\bar{1}\bar{2})$ from here on) surface pair was also investigated because its CuInSe_2 counterpart has been shown to be thermodynamically stable with particular combinations of defect(s) and growth conditions from DFT-LDA calculations [107, 108]. Eight different defect configurations of the surface pair were investigated. These are: a) The defect-free surface pair. b) Two Cu vacancies on the (112) surface. c) Cu, Fe vacancy pair on the (112) surface. d) Cu-on-Fe antisite on the (112) surface. e) Fe-on-Cu antisite on the $(\bar{1}\bar{1}\bar{2})$ surface. f) S-adatom on the $(\bar{1}\bar{1}\bar{2})$ surface. g) S-addimer on the $(\bar{1}\bar{1}\bar{2})$ surface. h) Cu, Fe vacancy pair at the (112) surface

and two S vacancies at the $(\bar{1}\bar{1}\bar{2})$ surface. Systems (b) to (g) were chosen because their CuInSe₂ counterparts were predicted to be stable based on calculations by Zunger and Jaffe, and Zhang and Wei [107, 108]. System (h) was constructed in order to maintain ‘macroscopic stoichiometry’ at both terminations based on the generalisation of surface polarity by Finnis [228].

For all surfaces and surface pairs, a constant slab thickness of roughly 10 Å was employed as that was shown to be sufficient to converge the formation energy of the (110) surface to within 0.01 Jm⁻².

The density functional calculations performed on the chosen surfaces followed the same procedure detailed in study of the bulk (Section 4.2). For non-stoichiometric configurations of the polar (112)/ $(\bar{1}\bar{1}\bar{2})$ surface pair, the surface formation energies were calculated within a grand canonical formulation. Defining the atomic chemical potential for each species (μ_{Cu} , μ_{Fe} and μ_{S}) relative to its pure bulk phase and in the limit of a low concentration of bulk defects, the surface formation energy of a slab E_{surf} is

$$E_{\text{surf}} = \Delta E + n_{\text{Cu}}\mu_{\text{Cu}} + n_{\text{Fe}}\mu_{\text{Fe}} + n_{\text{S}}\mu_{\text{S}}, \quad (5.1)$$

where

$$\Delta E = E_{\text{sys}} - NE_{\text{bulk}}(\text{CuFeS}_2) + n_{\text{Cu}}E_{\text{bulk}}(\text{Cu}) + n_{\text{Fe}}E_{\text{bulk}}(\text{Fe}) + n_{\text{S}}E_{\text{bulk}}(\text{S}). \quad (5.2)$$

Here, E_{sys} is the total energy of the slab, and $NE_{\text{bulk}}(\text{CuFeS}_2)$ is the energy of the equivalent amount of bulk CuFeS₂ with the same number of lattice sites and without any defects. $E_{\text{bulk}}(\text{Cu})$, $E_{\text{bulk}}(\text{Fe})$ and $E_{\text{bulk}}(\text{S})$ are the calculated bulk energy per atom of Cu(fcc), Fe(bcc) and S₈(molecule) respectively. n_{Cu} , n_{Fe} and n_{S} are the numbers of Cu, Fe and S atoms removed from the stoichiometric system to create the defects. For example, n_{Cu} , n_{Fe} and n_{S} are -1, +1 and 0 respectively for a surface with a single Cu-on-Fe antisite defect.

The existence of CuFeS₂ in chemical equilibrium constrains the sum $\mu_{\text{Cu}} + \mu_{\text{Fe}} + 2\mu_{\text{S}}$ to the heat of formation of CuFeS₂. We used the experimental value of -1.8 eV for the heat of formation obtained by Johnson and Steele [229]. Table 5.1 lists seven sets of μ_{Cu} , μ_{Fe} and μ_{S} values that were chosen to represent a wide range of growth conditions within this constraint. For each of the seven conditions, the surface formation of all

stable surface were computed and used, through the Wulff construction [170, 171], to predict an equilibrium crystallite morphology. The Wulff constructions were generated and visualised using the software package **DL-Visualise** [230].

Condition	$\mu_{\text{Cu}}/\text{eV}$	$\mu_{\text{Fe}}/\text{eV}$	μ_{S}/eV	Description
A	-1.8	0.0	0.0	Cu-poor
B	-0.9	-0.9	0.0	S-rich
C	-0.6	0.0	-0.6	Fe-rich
D	-0.45	-0.45	-0.45	Balanced
E	0.0	-1.8	0.0	Fe-poor
F	0.0	-0.6	-0.6	Cu-rich
G	0.0	0.0	-0.9	S-poor

Table 5.1: 7 sets of chemical potential values bound to the constraint $\mu_{\text{Cu}} + \mu_{\text{Fe}} + 2\mu_{\text{S}} = -1.8$ eV representing a wide range of reasonable growth conditions.

5.3 Results

5.3.1 Non-polar surfaces

The (110), (102) and (114) non-polar surfaces have surface energies of 0.58, 0.61 and 0.66 Jm⁻² respectively. The nature of the relaxations of these surfaces are found to have some general features in common; surface metal cations significantly displace inwards towards the bulk while surface anion species relax slightly outwards towards the surface. As an illustration, the unrelaxed and relaxed configurations of the (110) surface shown in Fig 5.2. This relaxation pattern serves to increase the stability of surfaces in two ways. First, it alleviates under-coordination of surface cations through enhanced metal-metal (Cu-Fe, Cu-Cu and Fe-Fe) interactions. Second, the tendency of the surface Cu and Fe cations to relax towards the bulk exposes S anions at the surface whose relatively large and polarisable electron clouds can provide electrostatic screening of the smaller metal cations. These general features of surface relaxation are typical for zinc-blende binary semi-conductors such as ZnO and have been reported in DFT-LDA calculations of CuInSe₂ [107, 108] and DFT-GGA calculations of CuFeS₂ [85]. For this class of materials, the (110) surface is found to be the most stable non-polar surface [109–111, 231]. This is consistent with the data presented here.

Configuration	Defect(s) on (112)	Defect(s) on $(\bar{1}\bar{1}\bar{2})$	A	B	C	D	E	F	G
(a)	None	None	0.61	0.61	0.61	0.61	0.61	0.61	0.61
(b)	$2 \times \text{Cu vacancies}$	None	0.33	0.61	0.71	0.76	0.90	0.90	0.90
(c)	Cu, Fe vacancy pair	None	1.02	1.02	1.21	1.16	1.11	1.21	1.30
(d)	Cu-on-Fe antisite	None	1.12	0.84	0.93	0.84	0.65	0.74	0.84
(e)	None	Fe-on-Cu antisite	0.22	0.50	0.41	0.50	0.69	0.60	0.50
(f)	None	S adatom	0.65	0.65	0.75	0.72	0.65	0.75	0.80
(g)	None	S addimer	0.53	0.53	0.72	0.67	0.53	0.72	0.82
(h)	S adatom	S vacancy	0.71	0.71	0.71	0.71	0.71	0.71	0.71
(110) surface	N/A	N/A	0.58	0.58	0.58	0.58	0.58	0.58	0.58

Table 5.2: Calculated surface energies of $(112)/(\bar{1}\bar{1}\bar{2})$ with the different defect configurations investigated at the seven growth conditions (A-G) defined in Table 5.1. The surface energy of the (110) surface, the most stable non-polar surface, is also shown for comparison. The surface energies are in Jm^{-2} . For each growth condition, the lowest surface energy is in bold.

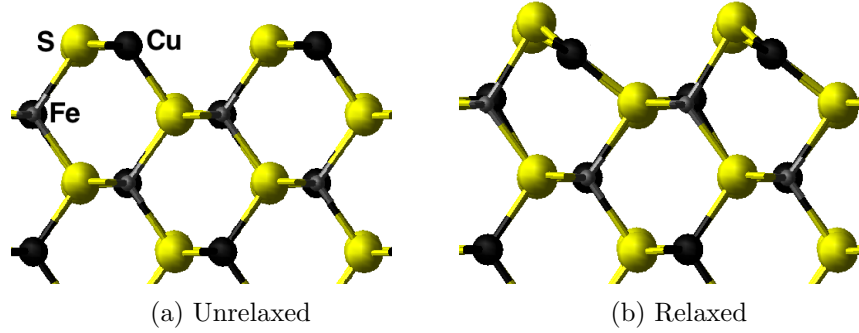


Figure 5.2: The unrelaxed (left) and relaxed (right) non-polar (110) surface. Copper, iron and sulphur atoms are coloured black, silver and yellow respectively. The (110) surface is at the top and the bulk like region is at the bottom.

5.3.2 The defect-free polar (112)/($\bar{1}\bar{1}\bar{2}$) surface pair

The defect-free configuration (configuration (a)) of the (112)/($\bar{1}\bar{1}\bar{2}$) surface pair has a surface formation energy of 0.61 Jm^{-2} which is similar to those calculated for the non-polar (110), (102) and (114) surfaces. While the stabilisation mechanism of the non-polar surfaces is mainly geometric, stabilisation of the (112)/($\bar{1}\bar{1}\bar{2}$) surface pair is attributed to a combination of geometric and electronic mechanisms.

The unrelaxed and relaxed configurations of the metal-terminated (112) surface are shown in Fig. 5.3. At the (112) surface, all 4 surface metal cations are displaced significantly ($\sim 0.80 \text{ \AA}$) into the bulk, while 2 of the S anions in the sub-surface layer relaxed outwards to the surface ($\sim 0.40 \text{ \AA}$), resulting in a partial swap of the unrelaxed surface and sub-surface layers. The purpose of the geometric relaxation at the (112) surface is similar to that of the non-polar surfaces; the coordination of the under-coordinated surface metal cations is increased and electrostatic screening of them is enhanced through exposure of S anions at the surface. Conversely, there is relatively little relaxation at the anion-terminated ($\bar{1}\bar{1}\bar{2}$) surface, which is unsurprising since the sub-surface metal cations are not under-coordinated and the geometry of the surface already facilitates electrostatic screening of the cations by S anions.

The electronic mechanism which stabilises the (112)/($\bar{1}\bar{1}\bar{2}$) surface pair involves charge transfer which is apparent in the density of states (DOS) plots and can be estimated using Mulliken population analysis. The total and projected DOS of bulk CuFeS_2 and that of the (112)/($\bar{1}\bar{1}\bar{2}$) surface pair are plotted in Fig. 5.4. The DOS of the surface pair are further projected onto atoms of the 4 repeating units (labeled in Fig. 5.3a) and shown in Fig. 5.5. The Fermi level is at 0.0 eV for all plots.

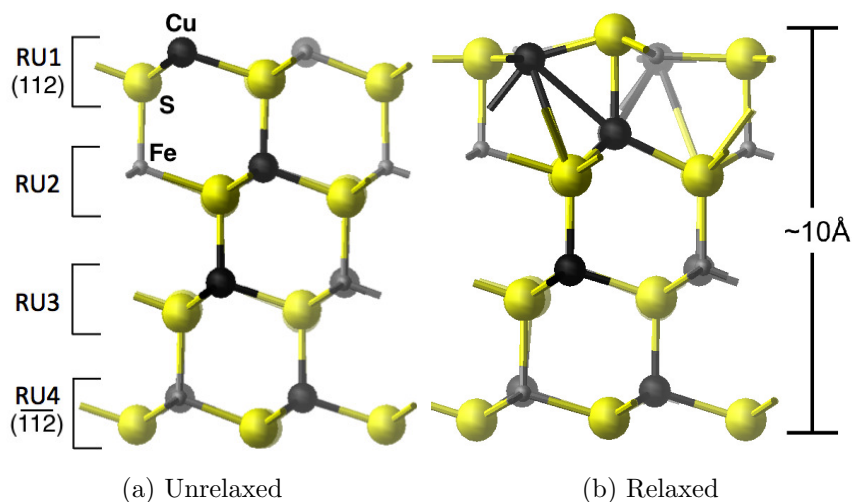


Figure 5.3: The unrelaxed (left) and relaxed (right) defect-free polar $(112)/(\bar{1}\bar{1}\bar{2})$ slab. Copper, iron and sulphur atoms are coloured black, silver and yellow respectively. The (112) surface is at the top while the $(\bar{1}\bar{1}\bar{2})$ surface is at the bottom. The 4 repeating units (RU) are also labeled.

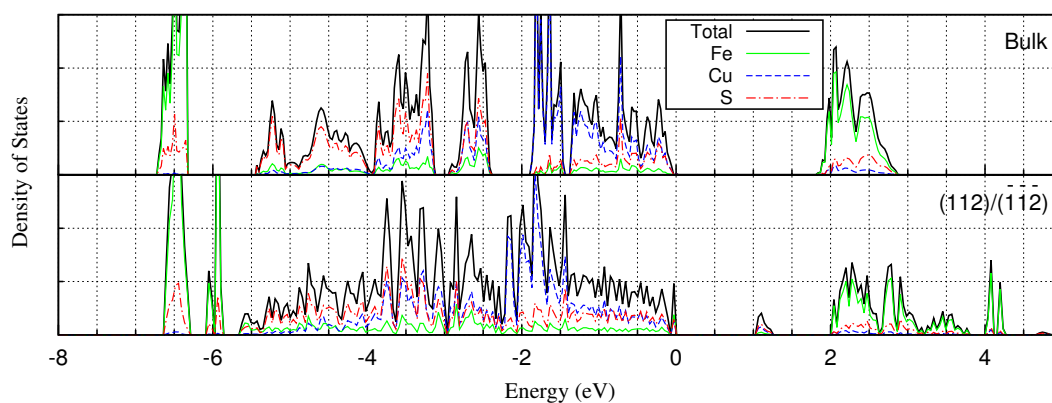


Figure 5.4: Total and projected density of states for bulk (top) and the $(112)/(\bar{1}\bar{1}\bar{2})$ surface pair (bottom) of CuFeS_2 . The DOS is projected onto Cu, Fe and S species. The Fermi level is at 0.0 eV.

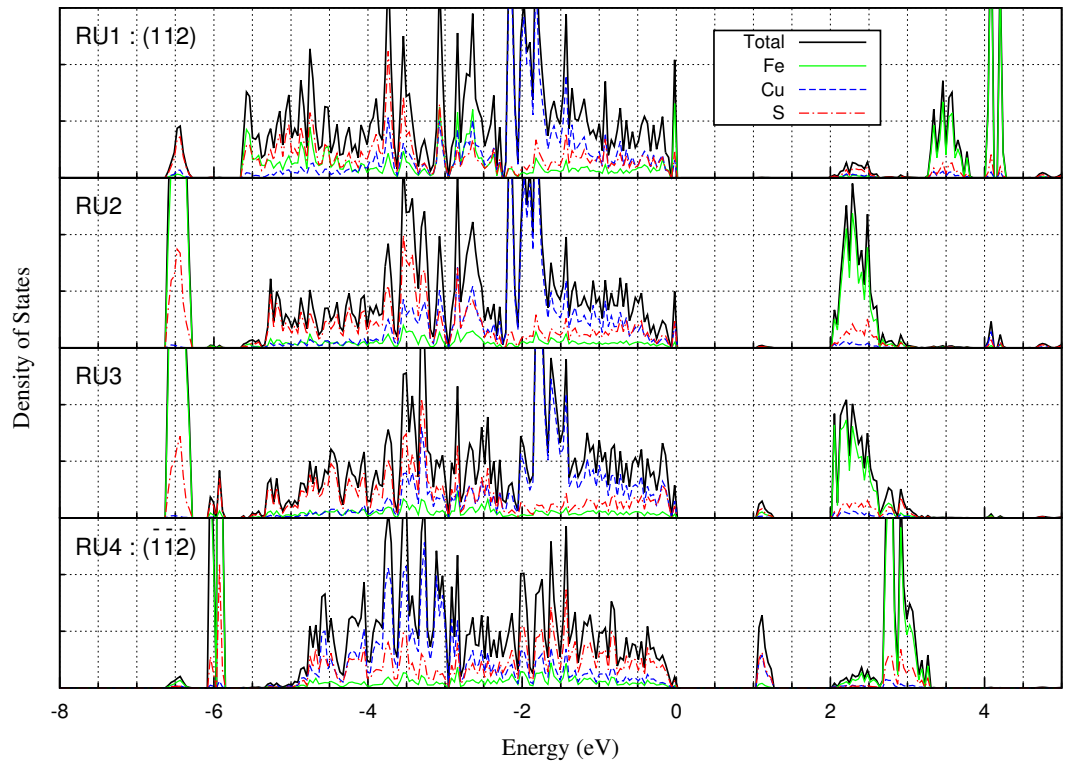


Figure 5.5: Total and projected density of states for each the 4 repeating units, defined in Figure 5.3a, of the (112)/($\bar{1}\bar{1}\bar{2}$) surface pair of CuFeS₂. The DOS is projected onto Cu, Fe and S species. The Fermi level is at 0.0 eV.

For bulk CuFeS_2 , the bottom of the conduction band consists of mainly empty $3d$ -Fe states, with a small contribution from $3p$ -S states. The corresponding occupied $3d$ -Fe states are in the range of -6.7 to -6.3 eV. The localised nature of these bands with little hybridisation indicates that Fe-S bonds are strongly ionic. The occupied $3d$ -Cu states are spread in the valence band between -4.0 eV and the Fermi level over several bands. A band of strongly ionic $3d$ -Cu states can be identified in the range of -1.8 to -1.4 eV. Another band, slightly hybridised with $3p$ -S states is present between -1.4 eV and the Fermi level. Finally, a couple of bands of $3d$ -Cu states strongly hybridised with $3p$ -S states are found in the range -3.9 eV to -2.4 eV. The mixture of ionic and hybridised states suggests that Cu-S bonds are only partially ionic.

For the polar $(112)/(\bar{1}\bar{1}\bar{2})$ surface pair the DOS of the middle two repeating units (RU2 & 3) have mostly retained the key features of the bulk crystal. One minor difference is the increased hybridisation of $3d$ -Cu and $3p$ -S states in the valence band, also observed in the surface repeating units (RU1 & RU4). This suggests a slight increase in the degree of covalency in Cu-S bonds. For the $(\bar{1}\bar{1}\bar{2})$ surface (RU4), the occupied $3d$ -Fe states are shifted up in energy by 0.5 eV compared with the bulk. This can be attributed to increased electrostatic repulsion due to contraction of surface Fe-S bonds and polarisation of the S electron cloud towards the bulk upon surface cleavage. At the (112) surface (RU1), the occupied $3d$ -Fe states shifts further up in the energy up to the valence band, which results in strong hybridisation with $3p$ -S and $3d$ -Cu states.

There are two key features in the DOS that, when considered in conjunction, provide evidence of charge transfer occurring across the surface pair. First, at the $(\bar{1}\bar{1}\bar{2})$ surface, band gap states consisting of a mixture of $3d$ -Cu and $3p$ -S states can be identified between 1.0 and 1.2 eV. Second, at the top of the valence band of the (112) surface a narrow band of $3d$ -Fe states, originating from the bottom of the conduction band in the bulk, can be observed. It is therefore reasonable to conclude that charge transfer occurs from the $(\bar{1}\bar{1}\bar{2})$ surface to the (112) surface, in particular from $(\bar{1}\bar{1}\bar{2})$ Cu and S atoms to (112) Fe atoms.

Mulliken population analysis allows numerical estimation of the charge transferred. Relative to the bulk, Fe species at the (112) surface gained on average 0.17 $|e|$ per atom while overall the surface as a whole (RU1) gained a total of 0.30 $|e|$ per unit cell. For the $(\bar{1}\bar{1}\bar{2})$ surface, S and Cu species lost 0.20 $|e|$ per atom and 0.03 $|e|$ per atom on average respectively, while the surface as a whole (RU4) lost a total of 0.83 $|e|$ per unit cell. Using the Mulliken charges calculated for the bulk system, a pure electrostatic argument predicts that a surface-to-surface charge transfer of 1.29 $|e|$ per unit cell across the slab is required to suppress the macroscopic electrostatic dipole in the surface pair.

As the estimated total charge transfer loss from atoms in the $(\bar{1}\bar{1}2)$ surface is close to this value, it can be concluded that stabilisation of the macroscopic field at the $(\bar{1}\bar{1}2)$ surface is indeed mostly electronic. The difference between the required and estimated charge loss from atoms in the $(\bar{1}\bar{1}2)$ surface to stabilise the macroscopic dipole can be accounted for by the imperfect ionicity of the system and possibly an additional stabilisation mechanism involving change in the degree of covalency in surface bonds.

To summarise, the $(112)/(\bar{1}\bar{1}2)$ surface pair is stabilised by a combination of geometric and electronic mechanisms. The geometric mechanism, localised to the (112) surface, involves significant geometry relaxation which exposes S anions that can then electrostatically screen the densely charged metal cations underneath. The electronic mechanism involves charge transfer predominantly from S species at the $(\bar{1}\bar{1}2)$ surface to Fe species at the (112) surface. Collectively, these processes serve to stabilise the surface pair by suppressing the electric dipole moment perpendicular to the slab, as illustrated in the plot of the computed planar averaged potential across the slab in Fig. 5.6. The plot shows that the gap between the potential at the (112) and $(\bar{1}\bar{1}2)$ surfaces, a measure of the electrostatic dipole across the surface, is almost eliminated during relaxation.

It should be emphasised that the surface energy is only well defined for non-polar surfaces, in other words surfaces which do not carry surface excess charge. For polar slabs, the surface energy linearly increases with the thickness of the slab due to the internal electrostatic field as a result of surface excess charge. Consequently, the fact there is still a non-zero dipole implies that the surface energy of the $(112)/(\bar{1}\bar{1}2)$ reported here is probably not meaningful. However, given that the (112) and $(\bar{1}\bar{1}2)$ surfaces have been observed to be thermodynamically stable for several other I-IV-VI $\text{Cu}(\text{In,Ga})(\text{S,Se})_2$ compounds isostructural to CuFeS_2 (see Section 2.3.3), it is reasonable to predict that the corresponding CuFeS_2 surfaces are likely to be stable as well. It is therefore assumed that in a macroscopic specimen of CuFeS_2 (112) and $(\bar{1}\bar{1}2)$ surfaces, stabilisation mechanisms in addition to those reported in this work, such as stoichiometric adjustment, are involved to neutralise the internal field.

5.3.3 The polar $(112)/(\bar{1}\bar{1}2)$ surface pair with defects

The data in Table 5.2 establishes that under most growth conditions, further stabilisation of the $(112)/(\bar{1}\bar{1}2)$ surface pair can be achieved with the formation of defects. With the exception of Fe-poor conditions (condition E), the $(112)/(\bar{1}\bar{1}2)$ surface pair with a Fe-on-Cu antisite on $(\bar{1}\bar{1}2)$ (configuration (e)) is lower in energy than its defect

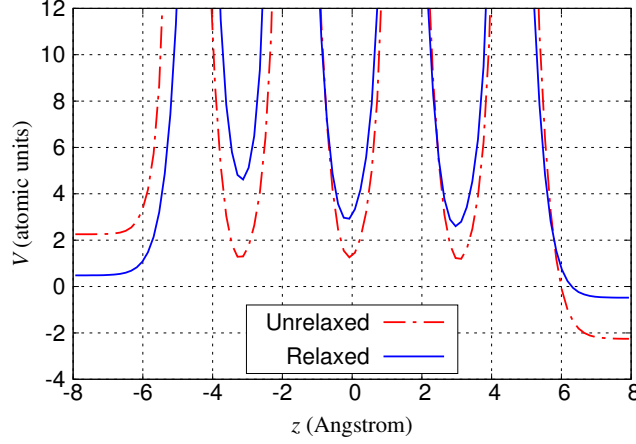


Figure 5.6: Planar averaged potential of the unrelaxed and relaxed defect free $(112)/(\bar{1}\bar{1}\bar{2})$ slab. The (112) surface is at positive z while the $(\bar{1}\bar{1}\bar{2})$ surface is at negative z .

free equivalent. Furthermore, the defect-stabilised surface pair is thermodynamically preferred over the non-polar (110) surface under those conditions apart from Cu-rich conditions (condition F). In particular, under Cu-poor conditions (condition A), its surface energy of 0.22 Jm^{-1} is the lowest out of all surface energies computed. The presence of an S-addimer at the $(\bar{1}\bar{1}\bar{2})$ surface (configuration (g)) also has a stabilising effect under Cu-poor, S-rich and Fe-poor conditions (conditions A,B & E). Under these conditions, the $(112)/(\bar{1}\bar{1}\bar{2})$ surface pair with a S-addimer at the $(\bar{1}\bar{1}\bar{2})$ surface is also thermodynamically preferred to the (110) surface. Out of all the defect configurations at the (112) surface investigated, only a pair of Cu vacancies (configuration (b)) stabilises the $(112)/(\bar{1}\bar{1}\bar{2})$ surface pair, and only under Cu-poor conditions (condition A). However, under these conditions, the surface energy is remarkably low at 0.33 Jm^{-1} . All the other defects studied did not give rise to additional thermodynamic stability of the $(112)/(\bar{1}\bar{1}\bar{2})$ surface pair, under any realistic environmental conditions. Fig. 5.7 is a ‘phase diagram’ which shows the most stable surface as a function of the atomic chemical potentials. It shows that except for Cu-rich conditions, the defect-stabilised $(112)/(\bar{1}\bar{1}\bar{2})$ surface pair is more stable than the (110) surface.

5.3.4 Surface morphology of CuFeS_2

Wulff constructions at growth conditions A-G of Table 5.1 were generated based on the surface energies calculated in this work. The (112) and $(\bar{1}\bar{1}\bar{2})$ surface energies are assumed to be equal to that calculated for the $(112)/(\bar{1}\bar{1}\bar{2})$ surface pair. Due to the fact

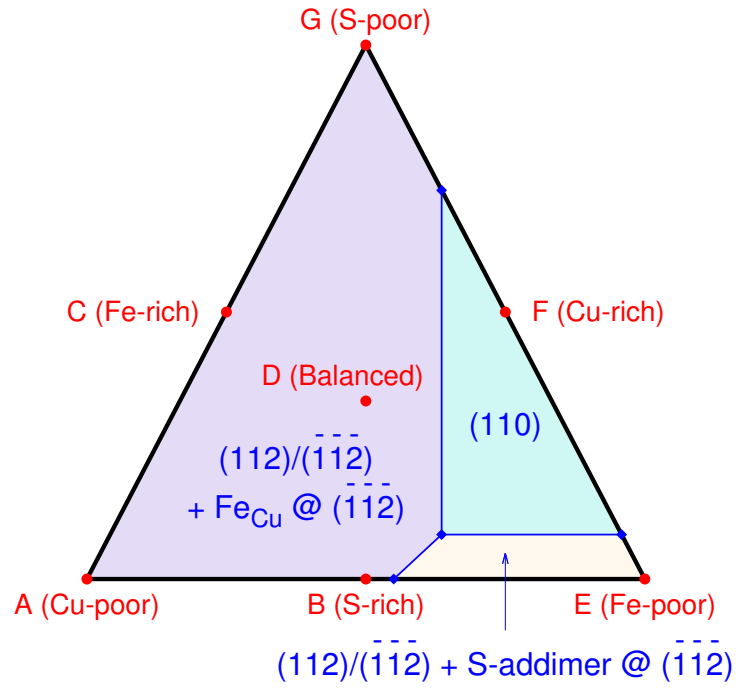


Figure 5.7: ‘Phase diagram’ showing the most stable surface (in blue) for all combinations of chemical potentials within the constraint $\mu_{Cu} + \mu_{Fe} + 2\mu_S = -1.8$ eV. The seven points (A-G) representing the growth conditions in Table 5.1 are marked in red.

	A	B	C	D	E	F	G
(110)	0.0	10.3	0.0	10.3	17.9	31.2	10.3
(102)	0.0	1.6	0.0	1.6	8.5	18.5	1.6
(114)	0.0	1.0	0.0	1.0	3.1	10.4	1.0
(112)/($\bar{1}\bar{1}\bar{2}$)*	100.0	87.2	100.0	87.2	70.5	39.8	87.2

Table 5.3: Proportional area (in %) of facets in the Wulff constructions created at the seven pre-determined set of atomic chemical potentials in Table 5.1. Note that for the (112)/($\bar{1}\bar{1}\bar{2}$) surface pair, the exact atomic configuration at the surface depends on the conditions (refer to Table 5.2).

that the surface energy of (112)/($\bar{1}\bar{1}\bar{2}$) is not meaningful because of the non-zero electrostatic dipole moment perpendicular to the surface, the Wulff constructions generated in this work are illustrative only. The proportion of different facets in the Wulff construction at growth conditions A-G of Table 5.1 is shown in Table 5.3. As the stability of the defect-stabilised (112)/($\bar{1}\bar{1}\bar{2}$) surface pair varies widely with respect to the (non-stoichiometric) defect(s) and hence the growth conditions, the surface morphology also depends heavily on the growth conditions. Under Fe-rich or Cu-poor conditions (conditions A & C) an Fe-on-Cu antisite defect at the (112) surface stabilises the (112)/($\bar{1}\bar{1}\bar{2}$) surface pair to such an extent that the Wulff construction predicts a crystallite exclusively formed of (112) and ($\bar{1}\bar{1}\bar{2}$) facets. Under Fe-poor conditions (condition E), the (112) and ($\bar{1}\bar{1}\bar{2}$) facets still have the highest proportional area, with decreasing, but non-negligible contributions from the non-polar (110), (102) and (114) facets. Cu-rich conditions (condition F) give rise to the ‘richest’ Wulff construction, with no family of facets having a proportional area of more than 40%. For the other 3 conditions (conditions B, D & G), the (112) and ($\bar{1}\bar{1}\bar{2}$) facets dominate, with a small combined contribution ($\sim 13\%$) from the non-polar surfaces. As an illustration of the strong influence that the growth conditions has on the surface morphology, the Wulff construction for copper rich and copper poor conditions are shown in Fig. 5.8. It should be noted the Wulff constructions are centro-symmetric because of the assumption that the surface energies of (112) and ($\bar{1}\bar{1}\bar{2}$) are equal, and in reality this is unlikely to be the case. From the data presented it is predicted that regardless of the growth conditions, defect stabilised polar (112) and ($\bar{1}\bar{1}\bar{2}$) facets are likely to form a significant portion of CuFeS_2 crystallites.

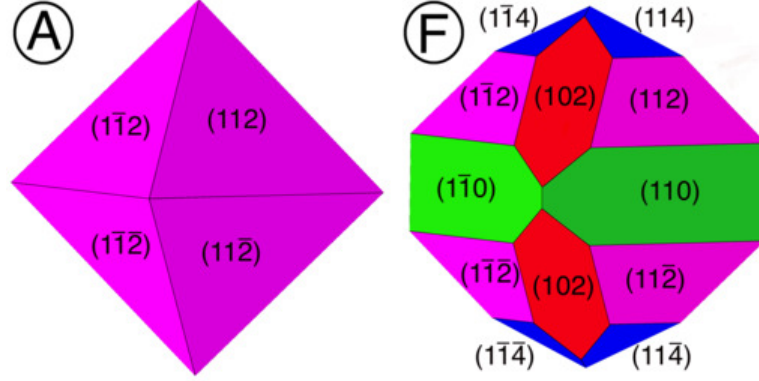


Figure 5.8: Wulff constructions of CuFeS₂ under growth conditions A (Cu-poor) and F (Cu-rich) defined in Table 5.1. Due to the symmetry of the system, (hkl) is equivalent to $(\bar{h}kl)$, $(h\bar{k}l)$ and $(h\bar{k}\bar{l})$.

5.4 Conclusions

This chapter presented an *ab initio* study of the crystallite morphology, surface composition and structure for a range of (1x1) CuFeS₂ surfaces as a function of the atomic chemical potentials. The calculations show that the (110) surface is the most stable non-polar surface with a surface energy of 0.58 Jm⁻², while the (102) and (114) surfaces are also low in energy (0.61 and 0.66 Jm⁻² respectively).

The relaxed polar defect-free (112)/(11̄2̄) surface pair was also found to be thermodynamically stable with a surface formation energy similar to the non-polar (110), (102) and (114) surfaces. The surface pair was stabilised during geometry relaxation due to a combination of electronic and geometric mechanisms that combine to suppress the electrostatic dipole perpendicular to the surface. Specifically, the (11̄2̄) surface was stabilised via transfer of charge to the (112) surface, while the (112) surface was additionally stabilised by a combination of geometric and electronic rearrangement.

The (112)/(11̄2̄) surface pair can be further stabilised by the formation of defects to an extent that makes it thermodynamically preferred over the non-polar (110) surface in the following scenarios: (a) Two copper vacancies at the (112) surface, under Cu-poor conditions. (b) A S-addimer at the (11̄2̄) surface, under Cu-poor, Fe-poor or S-rich conditions. (c) A Fe-on-Cu antisite at the (11̄2̄) surface, under all conditions except for Fe-poor or Cu-rich conditions.

Through Wulff constructions generated at a wide range of reasonable growth con-

ditions, it is concluded that within the bounds of this work, defect-stabilised (112) and $(\overline{112})$ facets will always form a significant constituent of the surface morphology regardless of the growth conditions. Understanding of the reactivity of these surfaces as well as (110), the most prominent non-polar surface, is therefore likely to be important to unravel the reasons behind the poor Cu dissolution kinetics. The next chapter will present an attempt at developing a QM/MM methodology for the purpose of studying Cu dissolution in which the low energy (110) and $(\overline{112})$ surfaces are used as model surfaces during testing of the methodology.

6

Development and Evaluation of a QM/MM Methodology

The study of Cu dissolution from CuFeS_2 requires a robust methodology that permits a reasonable representation of the relevant bulk (solid and liquid) environments while accurate enough to model charge transfer and other chemical processes. A hybrid QM/MM approach with electrostatic embedding is considered here as it can in principle achieve both these aims at a reasonable computational cost.

As discussed in Section 3.4.2, a surface can be represented using either a periodic or finite cluster model. The periodic model has the advantages that it can naturally model a bulk environment with a modest system size and is relatively simple to implement. However, most established QM codes are currently not capable of handling an infinite charge distribution, which would be required in periodic QM/MM electrostatic embedding. In addition, a large supercell may be required to prevent spurious interactions between repeated localised features such as defects from significantly impacting the accuracy of the model.

The finite cluster model completely avoids periodic artefacts and is often the only model available when using a QM/MM approach with electrostatic embedding. However, the model is relatively complicated due to careful treatment required to build an embedded cluster that accurately models long-range electrostatic interactions. In addition, the choice of the exact geometry of the cluster is not straightforward.

As the ultimate aim of the methodology is to study dissolution at a local site using a hybrid QM/MM approach with electrostatic embedding, the finite embedded cluster model is more appropriate and has been chosen for this study. Previously, in Chapter 5, the periodic model was used to study the surface morphology of CuFeS_2 . The results

from that investigation are therefore useful here as a benchmark for the finite embedded cluster model in order to critically assess its robustness. To ensure a valid comparison, the technical details, including the basis set and exchange-correlation functional, of the finite embedded cluster methodology employed here have been chosen to match those of the periodic methodology employed previously where possible.

The approach by Sokol *et al.*, described in Section 3.5.3 is used as the basis of the methodology developed in this chapter as it has already been successfully employed in studies of chemical processes on ionic surfaces. Although the approach has not been used for surfaces interfaced with a bulk liquid phase, there is no reason to suggest that this is not feasible, providing that solid-liquid interactions are carefully treated.

As no MM potential has been parameterised for the CuFeS_2 system, attempts were first made to develop one. However, as described later in Section 6.1.1, these attempts ultimately proved to be unsuccessful and instead a scheme was devised to represent the MM region by appropriately parameterised point charges on atomic sites.

In the first stage of the QM/MM methodology development, the (110) and $(\bar{1}\bar{1}\bar{2})$ surfaces were used as model systems for testing as they were identified to be stable low energy surfaces from the results of periodic B3LYP calculations presented in Chapter 5. To assess the reliability of the methodology, the electronic structure and optimised geometry computed on the embedded finite cluster system was compared with that previously computed on the periodic system. Cluster parameters such as the QM region size, MM region size and cluster size were systematically varied to determine optimal values for future calculations.

Following assessment of the performance of the methodology on gas phase surface systems, the second stage involved study of the adsorption of a single water molecule on the CuFeS_2 $(\bar{1}\bar{1}\bar{2})$ surface. Ultimately, it was concluded that the QM/MM methodology developed here was unsuited for studies of Cu dissolution in the $\text{CuFeS}_2\text{-H}_2\text{O}$ system. Nevertheless, the development process and testing of the methodology is documented comprehensively in this chapter as it may be useful for future developments to improve the methodology.

The rest of the chapter is organised as follows. In Section 6.1, the development of an embedded cluster QM/MM methodology, including the attempts at deriving a MM potential, is described. In Section 6.2, the procedure and scope of all the tests conducted to evaluate the methodology are detailed. In Section 6.3, results from the evaluation are presented and critical assessment of the suitability of the methodology for future studies of dissolution is given. Finally, Section 6.4 provides a summary of the chapter.

6.1 Methodology development

6.1.1 Development of a CuFeS_2 potential

As no MM potential has been derived specifically for the CuFeS_2 system, attempts were made to construct one for incorporation into the QM/MM methodology. The ReaxFF potential, was initially considered as the functional forms of its energy terms are designed to allow modelling of the formation and breaking of bonds and hence enable study of chemical reactions [120]. In addition, the ReaxFF potential in general aims to achieve transferability over different oxidation, chemical and physical states, which is particularly relevant for the study of charge transfer at a solid-liquid interface. This implies that if adequate parameters for the $\text{CuFeS}_2\text{-H}_2\text{O}$ system are available, the ReaxFF potential would in principle be a self-contained solution for large scale dynamical simulations of Cu dissolution, which is currently not feasible at the QM level of theory due to high associated computational cost. While it is unlikely that even a well parameterised ReaxFF potential would achieve the same accuracy as a fully QM or QM/MM approach, the results of ReaxFF simulations would nevertheless be useful to compliment results from calculations employing a higher level of theory.

The general strategy of parameterisation for the ReaxFF potential involves using relevant *ab initio* data to train parameter sets. As parameters for interactions between several relevant sets of elements, namely Cu/O/H [232], Fe/O/H [233] and Fe/S/O [234] already exist, not all interactions relevant to the $\text{CuFeS}_2\text{-H}_2\text{O}$ system needed to be parameterised. Following discussions with Adri van Duin, the main developer of the ReaxFF potential, a two-stage plan was devised to obtain a set of parameters for the $\text{CuFeS}_2\text{-H}_2\text{O}$ system. The first stage of the plan was to derive a set of parameters for the CuFeS_2 system solely, which involved:

1. Developing parameters for Cu-S interactions from equation of states of various $\text{Cu}_x\text{-S}_y$ phases (Cu_2S , CuS_2 , CuS and Cu_9S_5) and binding energies of S to the Cu (111) surface at various adsorption sites.
2. Developing parameters for Cu-Fe interactions from equations of states and heats of formation for various Cu_xFe_y alloys.

Once the parameters were validated through calculations on bulk CuFeS_2 , the second stage aimed to derive a set of parameters for the full $\text{CuFeS}_2\text{-H}_2\text{O}$ system. This involves developing parameters for Cu/S/O interactions from water binding energies and reaction barriers on Cu_xS_y surfaces. Unfortunately, significant difficulties were

encountered in the first stage of the process. In particular, the B3LYP methodology employed provided a poor description of the ground state electronic structure and energetics of several of the Cu_xS_y phases. In particular, Cu_9S_5 was predicted to be conducting when in reality it is a semiconductor, while the calculated Gibbs formation energy of Cu_2S had an error of over 20% compared to experiment [235]. Consequently, the pursuit of ReaxFF parameters for CuFeS_2 , let alone $\text{CuFeS}_2\text{-H}_2\text{O}$, was abandoned.

Apart from the ReaxFF potential, the parameterisation of simple two-body Lennard-Jones (LJ) 12-6 and Buckingham potentials for the CuFeS_2 system was also attempted. The functional form of the LJ 12-6 potential V_{LJ} as a function of atomic separation r is:

$$V_{\text{LJ}} = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right], \quad (6.1)$$

where ϵ and σ are parameters. For the Buckingham potential V_{Buck} , the functional form is:

$$E = Ae^{-r/\rho} - C/r^6, \quad (6.2)$$

where A , ρ and C are parameters.

In addition to parameters for bonded pair interactions (Cu-S and Fe-S), parameters of anion-anion interactions (S-S) were also derived. This follows the composition of ZnO potentials used in various surface embedded cluster studies [185,186,189]. To allow polarisation of the MM region to be described, the shell model of Dick and Overhauser was also considered for S anions via inclusion of a spring constant parameter describing the core-shell coupling. The total number of required parameters, excluding atomic partial charges, were 7 and 10 for the LJ 12-6 and Buckingham potentials respectively.

In contrast to the ZnO potentials used in the studies mentioned above, it is inappropriate to use formal charges for the MM partial charges in the CuFeS_2 potential as analysis of the bulk density of states in Chapter 4 showed that CuFeS_2 has significant covalent character. However, to prevent the numerical procedure of the parameterisation process from being too complex because of the simultaneous fitting of too many parameters, the charges were not allowed to vary during parameterisation.

Instead, sets of partial charges were constructed systematically such that Cu had a partial charge between +0.1 and +1.0 e , Fe had a partial charge between +1.0 and +3.0 e , and the partial charge of S was deduced to enforce neutrality of the system. For each set of constant partial charges, the unknown parameters were fitted to reproduce a range of structural and physical observables, including lattice constants, elastic constants, the bulk modulus and dielectric constants. The parameterisation was performed in the software package GULP [236,237].

For each set of partial charges, the strength of the fit was judged by the weighted “sum of squares” quantity, F , calculated as:

$$F = \sum_{i}^{\text{all observables}} [w_i(O_i^{\text{MM}} - O_i^{\text{Ref.}})^2], \quad (6.3)$$

where O_i^{MM} is observable i calculated using the interatomic potentials and $O_i^{\text{Ref.}}$ is the corresponding reference value, which in this work was calculated using DFT-B3LYP. As in general the lower the final sum of squares the better the potential, the parameterisation process involved varying the parameters to minimise F .

There are two main factors which governed the choice of the weighting factors w_i in this work. First, the properties that the potential parameters are fitted to have numerical values that differ significantly in magnitude. For example, the elastic constants c_{11} and c_{33} in GPa are around 10 times larger in magnitude than the dielectric constants ϵ_{11} and ϵ_{33} . The initial weighting factors were therefore chosen such that equivalent proportional differences in the calculated and reference values result in roughly equal contributions to the sum of squares quantity. Second, the reliability of the QM reference values for different properties also differ; lattice constants are generally more reliable than elastic or dielectric constants. The weighting factors were therefore adjusted such that the fitting is more biased to accurately reproduce the lattice constants. The fitting process involves determination of the set of parameters that minimises the weighted sum of squares. The optimal partial charges were those that resulted in the best fit to the observables after parameterisation, in other words those that gave the lowest sum of squares quantity.

For both potential forms considered, the results of the parameterisation were similar. It was relatively straightforward to obtain parameters that reliably reproduced the bulk properties of CuFeS_2 . However, when these potentials were subsequently employed for relaxation of the DFT-B3LYP optimised (110) slab, the resulting geometry differed significantly to the initial geometry. Differences between the MM and QM optimised geometry include large distortions ($> 50\%$) of bond lengths, and complete loss of the surface atomic structure. Attempts were made to refine the potentials with the aim of reproducing the surface geometry, but ultimately this did not result in significant improvement of the MM relaxed geometry. It was therefore concluded that the potentials were not suited to be employed in the QM/MM methodology. It is possible that the difficulty in parameterising a robust potential for CuFeS_2 is due to complexities arising from the presence of two rather than one cationic species in addition to the fact that

CuFeS₂ is a semi-ionic compound.

6.1.2 Point charge model for the MM region

Following unsuccessful attempts at deriving interatomic potentials for CuFeS₂, a simpler point charge model was instead considered for the MM region. In this model, each MM atom is represented by a point charge and no interatomic potential terms are included. The justification of this model is based on the fact that in an ionic material electrostatic interactions are dominant relative to other types of interactions. It is therefore argued that the neglect of other interactions, which mostly describe short-range effects, is unlikely to have a substantially detrimental effect on the accuracy of the methodology for the region immediately about the cluster origin, provided that the QM region is sufficiently large.

Formal charges are not representative of atomic partial charges in CuFeS₂ due its considerable covalent character. The magnitudes of the point charges were therefore carefully assigned to establish a robust representation of the electrostatic interactions through reproduction of the QM electrostatic potential. During optimisation of the charge magnitudes, comparison of the electrostatic potential computed using the classical point charge model and QM model was only performed above the surface and not within the surface due to the difference in the charge distribution between the two models. In the QM model an atom is a positive nucleus surrounded by diffuse negative electron charge, while in the classical point charge model it is a single point charge carrying an effective net atomic charge. As the collective ionic volume accounts for most of the volume within CuFeS₂, it is inappropriate to compare the electrostatic potential computed under the two models in the interatomic region within CuFeS₂.

Calculation of the QM (keyword `POT3`) and classical (keyword `CLAS`) electrostatic potentials were performed within the `CRYSTAL09` code. The QM electrostatic potential was calculated as the potential of an atom centred multipolar decomposition of the charge density, which was defined from Mulliken analysis. The classical electrostatic potential was calculated as the potential due to a set of atom centred point charges with user defined charge magnitudes.

The point charge magnitudes were parametrised separately for the (110) and ($\bar{1}\bar{1}\bar{2}$) surfaces. As a starting point, the classical electrostatic potential was calculated using Mulliken charges obtained from previous DFT-B3LYP calculations. For both surfaces, the electrostatic potential sampling grid consists of 37 layers along the z-axis (perpendicular to the surface) separated by 5/6 Bohr (≈ 0.44 Å). Each layer consists of a

2-dimensional grid with 16 equally spaced points parallel to the a surface unit vector and a number of points parallel to the b surface unit vector such that the spacing between points is roughly the same along both directions. In total there were 9472 grid points ($16 \times 16 \times 37$) for the (110) surface and 11248 grid points ($16 \times 19 \times 37$) for the $(\bar{1}\bar{1}2)$ surface. For the (110) surface, the first layer was 3.03 Å away from the surface (defined to be the z -coordinate of the outermost atom), while for the $(\bar{1}\bar{1}2)$ the first layer was 2.52 Å away from the surface. The final layers were 18.90 and 18.40 Å away from the (110) and $(\bar{1}\bar{1}2)$ surfaces respectively.

Figures 6.1a and 6.1b are scatter plots of the classic electrostatic potential against the QM electrostatic potential covering all grid points for (110) and $(\bar{1}\bar{1}2)$ respectively. In figures 6.2a and 6.2b the same data is presented except the classical and QM electrostatic potential at each grid point is plotted separately against the perpendicular distance from the surface. The following observations can be made from the plots:

1. The overall QM electrostatic potential above the surface is reproduced more accurately for (110) compared to $(\bar{1}\bar{1}2)$. This is explained by considering the polarity of the two surfaces. The (110) surface is Tasker type 1 non-polar which means the (unrelaxed) atomic layers are neutral and therefore the electrostatic potential outside the surface is expected to be zero. As the total charge of the system is zero, the neutrality of the atomic layers is mostly upheld by the Mulliken charge magnitudes. The zero electrostatic potential is therefore reproduced with only small errors. Conversely, the electrostatic potential above the nonpolar $(\bar{1}\bar{1}2)$ is not expected to be zero outside of the surface. As the Mulliken charges are heavily dependent on the basis set, it is therefore unlikely that the QM electrostatic potential is reproduced.
2. For the case of $(\bar{1}\bar{1}2)$, the difference between the classical and QM electrostatic potential values, particularly at large distances away from the surface, is mostly accounted for by a constant shift of around 0.032 atomic units.
3. Closer to the surface, the larger the variation in the electrostatic potential across the grid points. This is explained by considering that the contribution of a point charge to the electrostatic potential at a point in space is inversely proportional to the distance between them. Consequently, the effect of the local surface charge distribution will have a larger influence on the electrostatic potential closer to the surface.
4. For the (110) surface, the classical potential becomes increasingly non-zero away

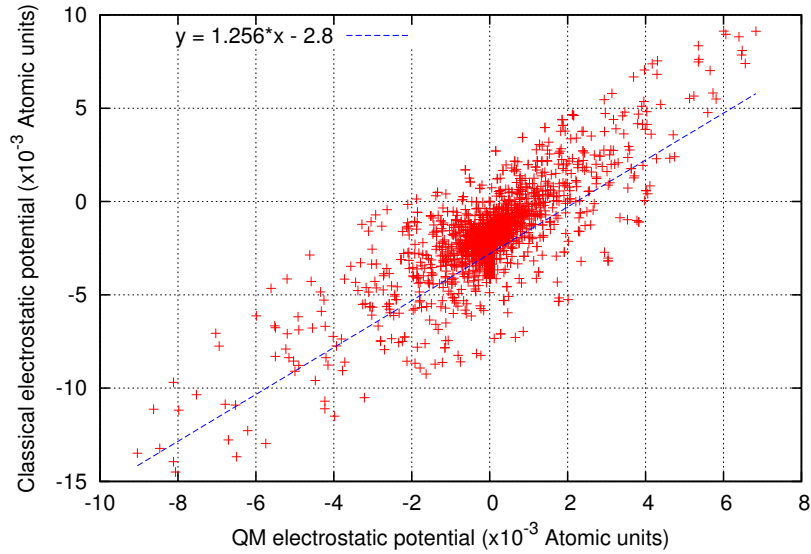
form the surface. However, this is not the expected behaviour as the surface is non-polar and hence there is no net electrostatic field outside the surface. This behaviour was later found out to be due to a slight slab net charge of $0.0007e$ arising from the rounding of Mulliken charges. The same was found to be the case for the $(\bar{1}\bar{1}2)$, but to a lower extent as the slab net charge was $0.00035e$.

It is apparent that the difference between the classical and QM electrostatic potential values of the $(\bar{1}\bar{1}2)$ surface is mostly accounted for by a constant scale factor. This is verified in Figure 6.3, which shows the effect of applying different scaling factors to the Mulliken charges in computing the classical potential. The scale factor which results in an optimal reproduction of the QM electrostatic potential was deduced by determining the classical-to-QM ratio of the potential away from the surface and determined to be roughly 0.35.

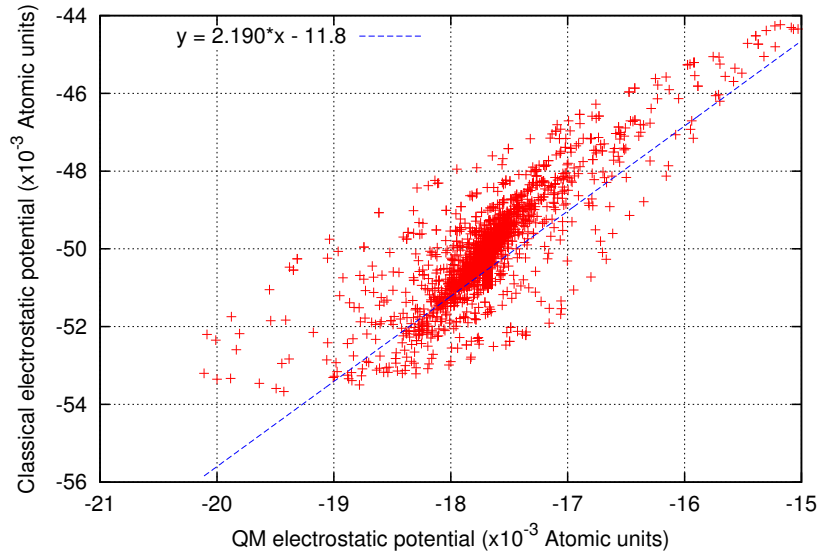
Figure 6.4 shows a scatter plot of classical against QM electrostatic potential values for all grid points using this optimal scaling factor. Through comparison with Figure 6.1b, it is clear that this charge scaling results in significantly more accurate representation of the QM electrostatic potential. A least squares fit of $y = cx$, where c is a constant, has been performed on the scatter data in Figure 6.4. The best fit value for the constant c , shown visually in the figure, is 0.999 (≈ 1.000), which provides further validation of the optimal scaling factor. A plot of the difference between the classical and QM electrostatic potential, in other words the electrostatic potential error, for all grid points against perpendicular distance is shown in figure 6.5. The plot shows that the largest errors occur at grid points closest to the surface, corresponding to the first layer of the sampling grid, and have a value of roughly 0.002 atomic units. The largest error corresponds to the presence of extra charge with magnitude $0.01e$ at a distance 3 Å away from the grid point. However, the plot also shows that near the surface the maximum error increases exponentially with decreasing distance to the surface. The large errors close to the surface is a direct manifestation of the difference in the distribution of charge density between classical (point charge) and QM descriptions (nucleus & electronic wavefunction).

This is confirmed by analysing the electrostatic potential for a single ion. Figure 6.6a compares the classical and QM electrostatic potential for S^{2-} as a function of r , the distance away from the anion. The figure also shows the classical electrostatic potential against r for a point charge with +16 charge, accentuating the difference between the classical and QM models. In the classical model, the anion is a point charge with a charge of $-2e$, which means that the electrostatic potential, V_E , as shown in Figure 6.6a,

Figure 6.1: Scatter plots of classical vs. QM electrostatic potential for all grid points above the surface for (110) and $(\bar{1}\bar{1}\bar{2})$. The classical electrostatic potential was calculated from unscaled Mulliken charges. The best fit linear line is shown in each plot.

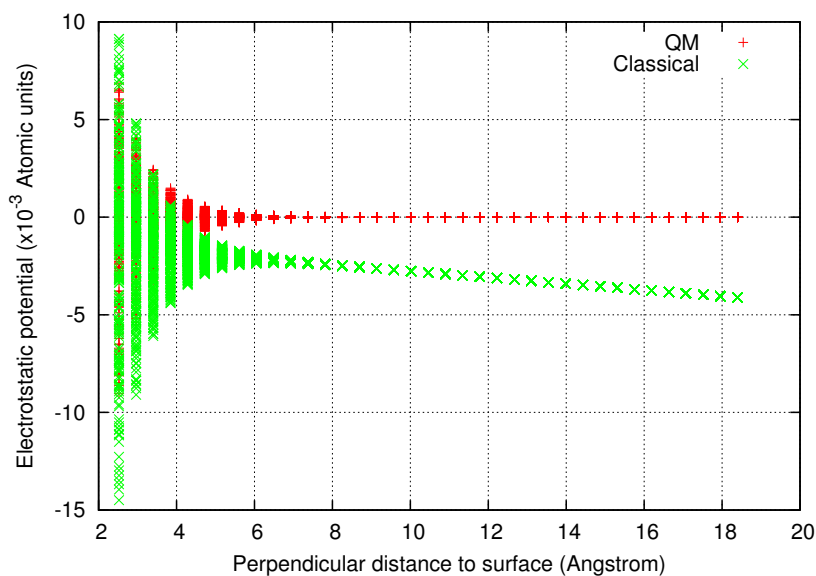


(a) Scatter plot for the (110) surface.

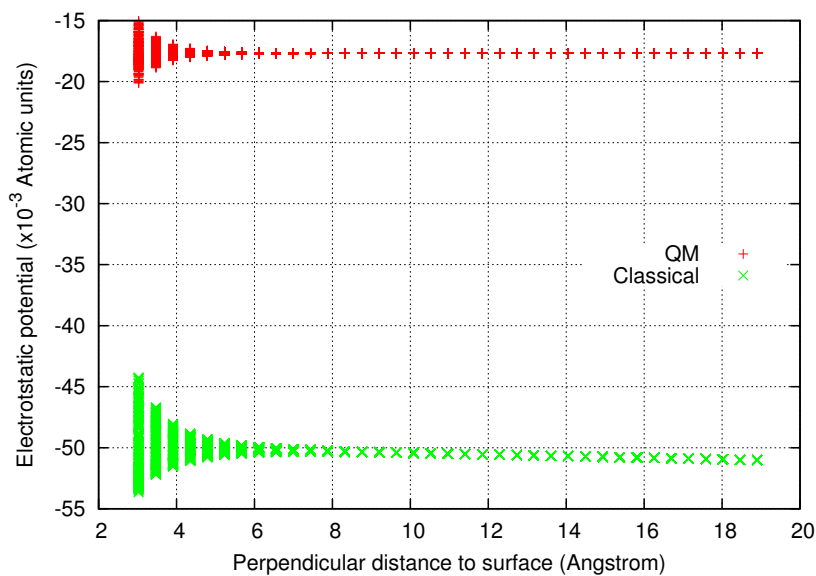


(b) Scatter plot for the $(\bar{1}\bar{1}\bar{2})$ surface.

Figure 6.2: Plots of classical and QM electrostatic potential at all grid points against perpendicular distance from the surface. The classical electrostatic potential was calculated from unscaled Mulliken charges.



(a) Plot for the (110) surface.



(b) Plot for the $(\bar{1}\bar{1}2)$ surface.

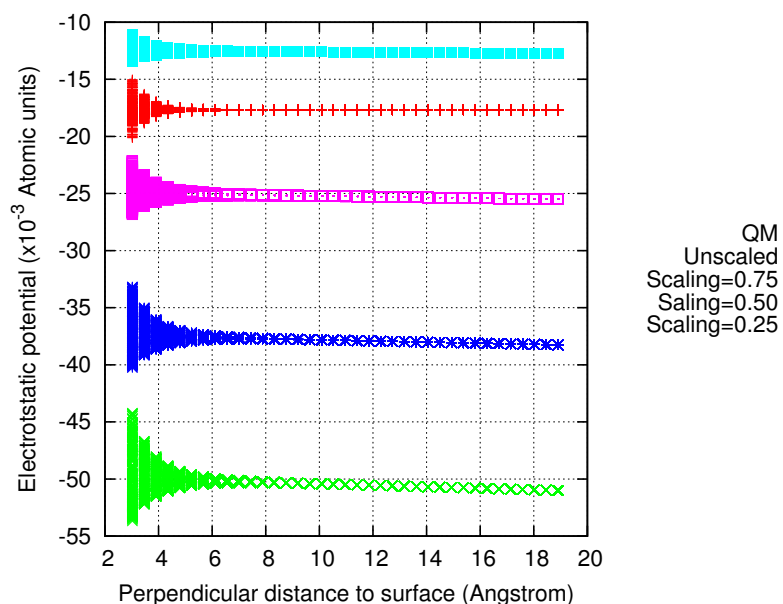


Figure 6.3: Plot of classical electrostatic potential at all grid points calculated using Mulliken charges with a range of scaling factors for the $(\bar{1}1\bar{2})$ surface. The potential values are plotted against perpendicular distance from the surface. The corresponding QM electrostatic potential is shown as reference.

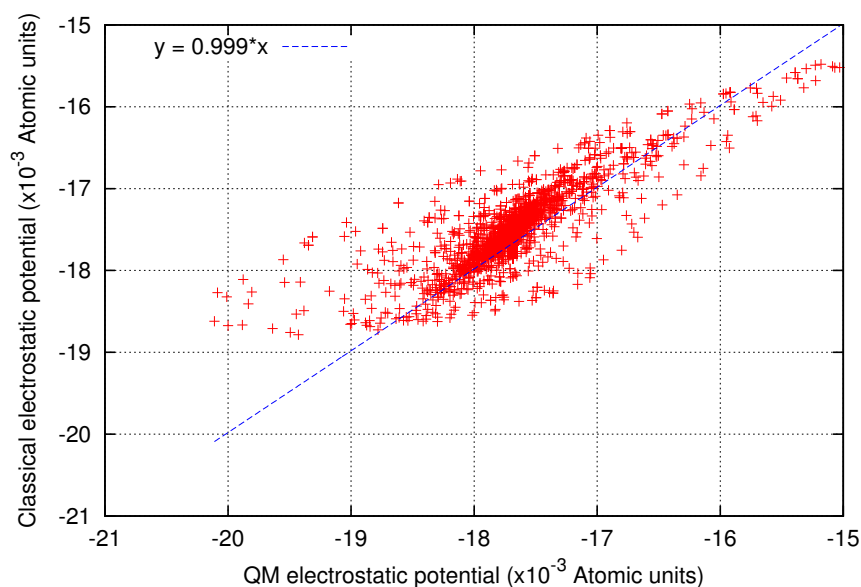


Figure 6.4: Scatter plot of classical vs. QM electrostatic potential at all grid points for the $(\bar{1}1\bar{2})$ surface. A Mulliken charge scaling factor of 0.35 is used for to compute the classical electrostatic potential. The best fit linear line is shown.

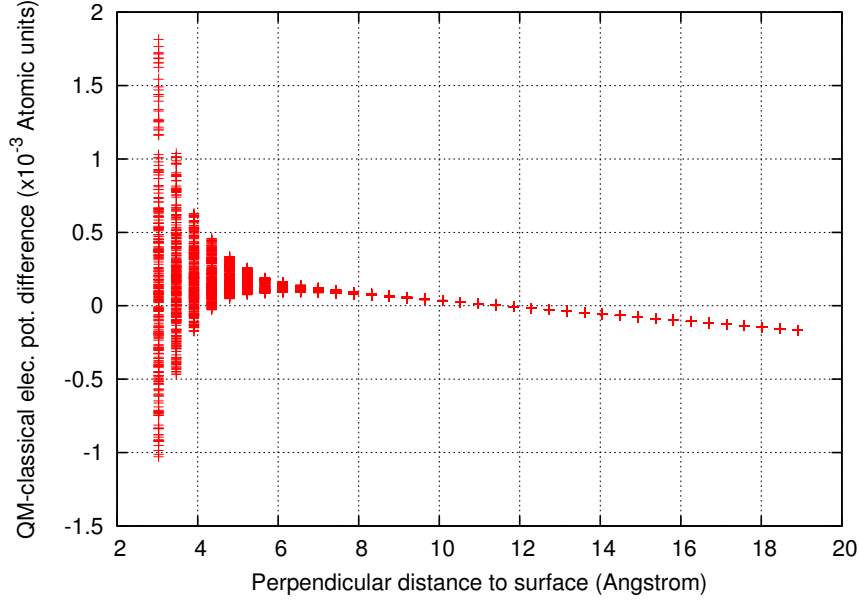


Figure 6.5: Difference between classical and QM electrostatic potential at all grid points for the $(\bar{1}\bar{1}2)$ surface. A Mulliken charge scaling factor of 0.35 is used to compute the classical electrostatic potential.

varies via the equation

$$V_E = \frac{1}{4\pi\epsilon_0} \frac{Q}{r}, \quad (6.4)$$

where ϵ_0 is the vacuum permittivity, Q is the charge ($-2e$) and r is the distance to the anion. In the QM model, the anion is described as a positive nucleus ($Q = +16e$) surrounded by a negative electronic wavefunction ($Q = -18e$). Since the charge density is spherically symmetric, the electrostatic potential at distance r from the nucleus is only dependent on the charge within the spherical region centred at the nucleus with radius r . The electrostatic potential is therefore highly positive at small r close to nucleus as little negative charge is within the “inner sphere”. As r increases, the electrostatic decreases rapidly to a maximum negative value at $r \approx 1.5$ Å. This is a combination of an increasing distance to the positive nucleus with the rapid inclusion of negative charge in the inner sphere. As r increases further, the anion appears closer and closer to a point charge and the QM electrostatic potential converges to the classical one. Figure 6.6b plots the difference between the classical and electrostatic potential as a function of r . Through comparison with Figure 6.5, it is concluded that within ~ 3.5 Å from the surface the error due to the classical point charge approximation dominates. This suggests that 3.5 Å as a lower bound for the radius of the QM region in the

QM/MM methodology developed in this chapter.

For the (110) surface, the choice of an optimal scaling factor is less straightforward in part because of the error arising from the non-zero net charge of the slab. In addition, as seen in Figure 6.7, variability of the electrostatic potential for points near the surface is highly sensitive to the scaling factor. An optimal scaling factor for the Mulliken charges of (110) was determined based on a quantity representing the overall error in the classical electrostatic potential. This quantity, denoted ϵ , is defined as:

$$\epsilon = \sqrt{\sum_i^{\text{grid points}} \left(V_i^{\text{Classical}} - V_i^{\text{QM}} \right)^2}, \quad (6.5)$$

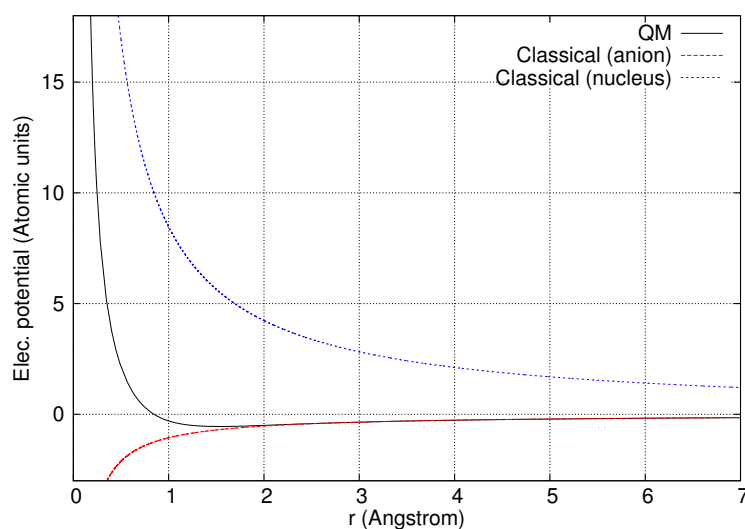
where $V_i^{\text{Classical}}$ and V_i^{QM} are the classical and QM electrostatic potentials at grid point i , respectively. ϵ is equivalent to the root-mean-square (rms) of the difference between the classical and QM electrostatic potential for all grid points. All scaling factors between 0.00 (representing no MM charges) and 1.00 (original Mulliken charges) in increments of 0.05 were considered. The optimal scaling factor was determined to be the one that minimises ϵ .

Figure 6.8 plots the rms error, ϵ of the classical electrostatic potential covering all grid points against scaling factor. The results suggest that the optimal scaling factor is 0.05, much lower than the optimal scaling factor for the $(\bar{1}\bar{1}2)$ surface. However, this is an underestimation due to the need to reproduce the long-range (zero) QM electrostatic potential, which is not replicated under the classical model due to the non-zero net charge of the slab. As the ultimate purpose of the QM/MM methodology is to study surface chemistry, it is far more vital to reproduce the correct electrostatic potential closer to the surface.

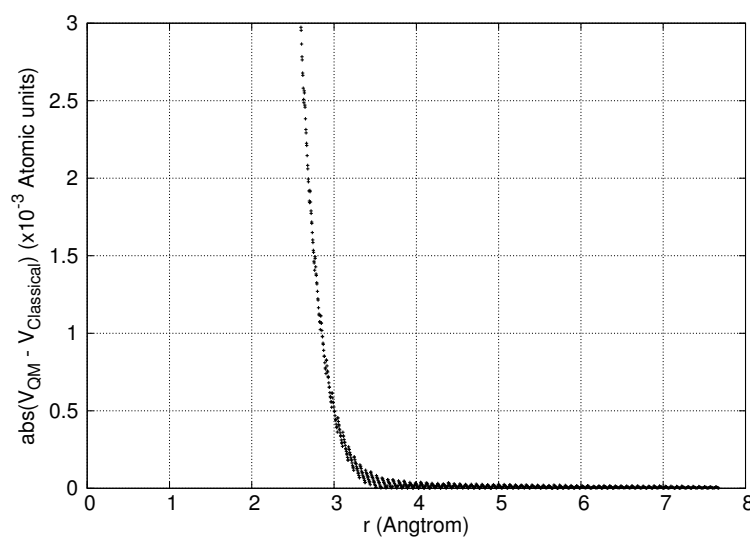
To identify a more suitable scaling factor, a threshold distance was set at 3.85 Å, equal to the average distance from an atom to its second nearest neighbour in bulk CuFeS₂. Each point of the sampling grid was categorised into the “near” or “far” region depending on whether the distance from that point to the closest (surface) atom was less than or above the threshold distance. The rms error of the classical electrostatic potential was calculated separately for the near and far regions, denoted as ϵ_{near} and ϵ_{far} respectively. The near region consisted of 5.5% (518 out of 9472) of the total grid points while the far region consisted of the remaining 94.5%.

A second method was employed to determine a suitable scaling factor. In this method, the whole grid was considered but instead of treating all points equally, a weighted rms error, $\epsilon_{\text{weighted}}$ was calculated according to equation 6.6:

Figure 6.6: Comparison of classical and QM electrostatic potential due to a S^{2-} anion as a function of the distance to the anion.



(a) Plot with classical and QM electrostatic potentials plotted together.



(b) Plot of the difference between the classical and QM electrostatic potentials.

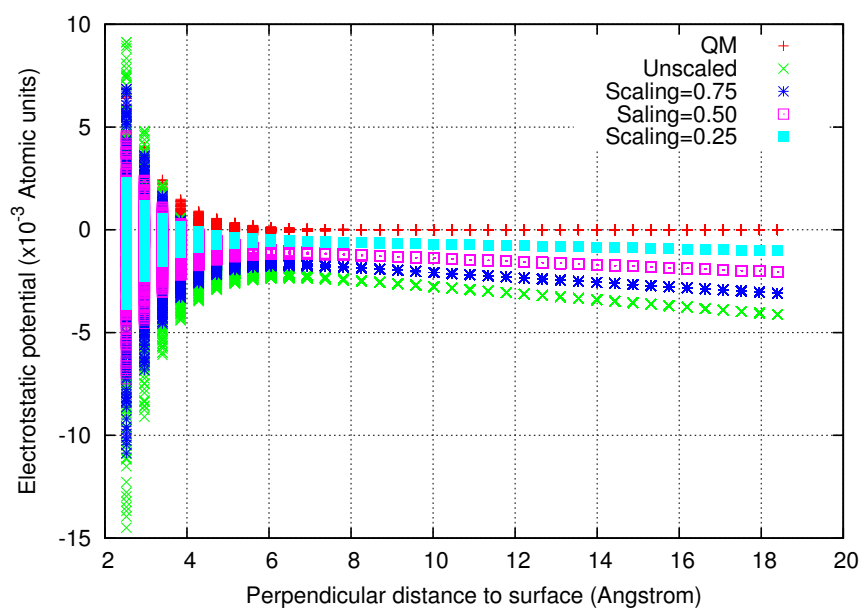


Figure 6.7: Plot of classical electrostatic potential at all grid points calculated using Mulliken charges with a range of scaling factors for the (110) surface. The potential values are plotted against perpendicular distance from the surface. The corresponding QM electrostatic potential is shown as reference.

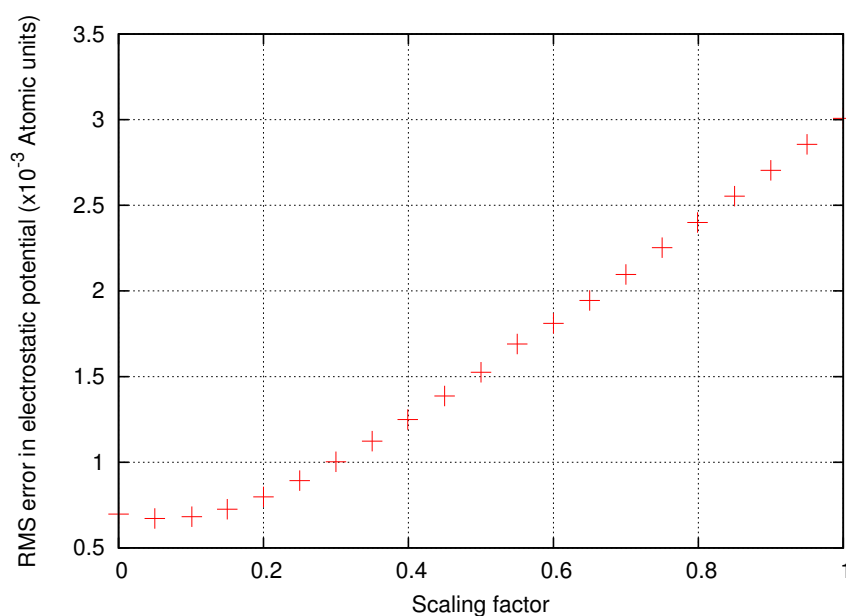


Figure 6.8: Plot of the overall RMS error of the classical electrostatic potential compared to the corresponding QM potential for (110) against scaling factor.

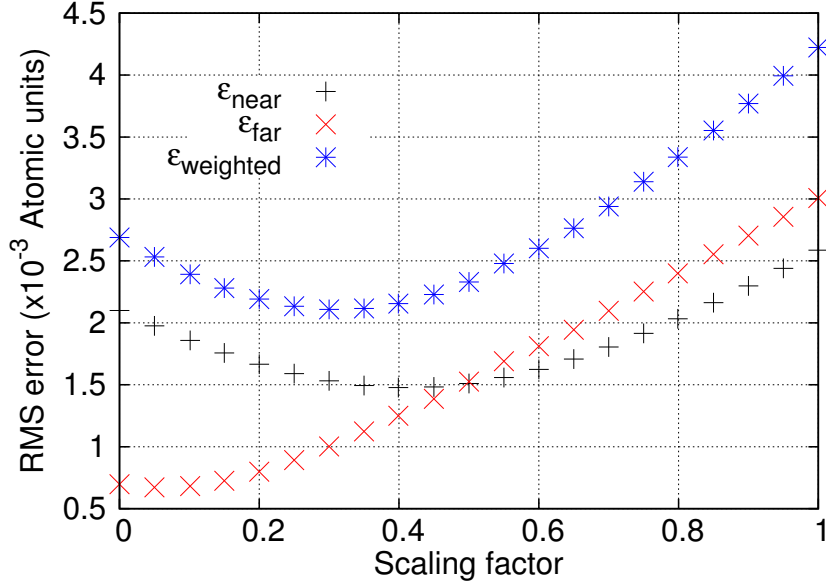


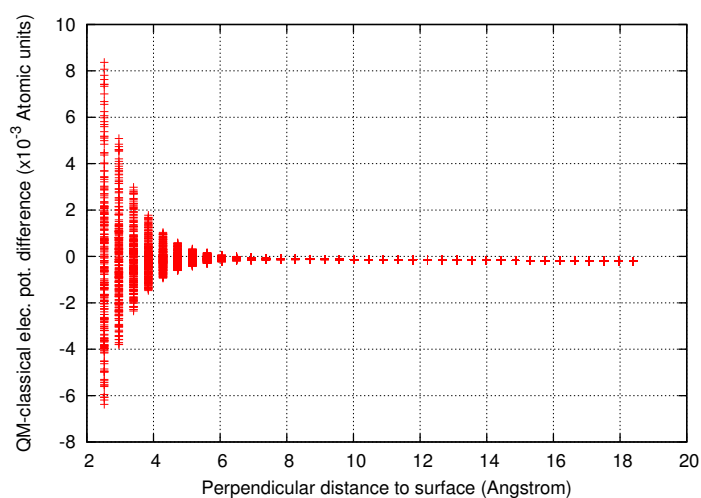
Figure 6.9: Different RMS errors of the classical electrostatic potential for the (110) surface against Mulliken charge scaling factor.

$$\epsilon_{\text{weighted}} = \sqrt{\sum_i \left[\frac{\bar{r}}{r_i} \left(V_i^{\text{Classical}} - V_i^{\text{QM}} \right) \right]^2}, \quad (6.6)$$

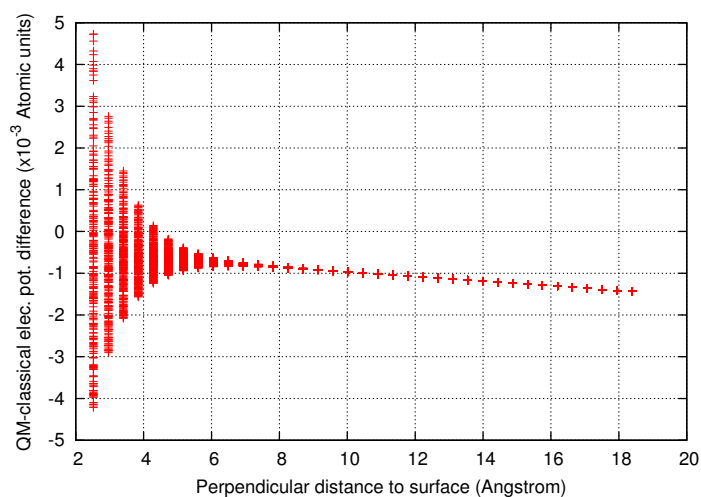
where the sum is over all grid points i , $\bar{r}$ is the mean distance from all grid points to its respective closest atom and r_i is the distance from grid point i to the closest atom. The computed ϵ_{near} and $\epsilon_{\text{weighted}}$ values, which both bias the grid points close to the surface, suggest optimal scaling factors of around 0.40 and 0.30 respectively. The variation of the rms errors ϵ_{near} , ϵ_{far} , and $\epsilon_{\text{weighted}}$ with scaling factor is plotted in Figure 6.9.

Figures 6.10a and 6.10b show the error of the classical electrostatic potential over all grid points for scaling factors of 0.05 and 0.35 respectively. The figures show that a scaling factor of 0.35 significantly improves upon the electrostatic potential close to the surface, at the expense of a slowly increasing error as the distance from the surface increases. As it is more important to reproduce the QM electrostatic potential close to the surface, a scaling factor of 0.35, coincidentally the same factor used for the $(\bar{1}\bar{1}2)$ surface, was employed during testing of the QM/MM methodology on the (110) surface.

Figure 6.10: Plot of the difference between classical and QM electrostatic potential at all grid points against perpendicular distance from the surface for (110).



(a) Mulliken charge scaling factor = 0.05.



(b) Mulliken charge scaling factor = 0.35.

6.2 Evaluation of the methodology

6.2.1 Overall approach

The robustness of the QM/MM methodology was assessed by determining whether electronic and geometric properties computed previously using the periodic QM approach could be reproduced under the QM/MM finite cluster approach. The influence of a wide range of elements of the cluster system on the accuracy of the methodology was systematically studied. Elements which are specified by a number, which are henceforth referred to as cluster parameters, are:

1. Cluster size, specified by the cluster radius.
2. QM region size, specified by the number of coordination shells about the cluster origin Cu atom. The QM region size implicitly defines the MM (point charge) region.
3. Active region size, only relevant for optimisations, specified by the number of coordination shells about the Cu origin.
4. Scaling factor of the MM charges. This is multiplied to the corresponding Mulliken charge of the periodic system to give the magnitude of the MM charges.

Other, non-numerical elements are:

1. The presence of MM point charges and the embedding point charges.
2. Reference charges used to parameterise the embedding point charges.
3. The inclusion of an interface region consisting of cationic pseudopotentials.

In the first stage of testing single point calculations and geometry optimisation were performed on clusters representing the (110) and $(\overline{11}2)$ surfaces of CuFeS_2 . Each cluster element identified above was studied independently, by keeping everything else constant, to determine its contribution to the accuracy of the methodology. The sensitivity and convergence of the results to change in the cluster parameters was also investigated.

The single point calculations were performed on the optimised geometry obtained from the periodic QM calculations reported in Chapter 5. These were used to assess the accuracy of the resulting electronic properties, in terms of the Mulliken charges and density of states (DOS). As the cluster system is finite, an effective density of states (EDOS) were computed via the following procedure:

1. Extract the eigenvalues of the spin-up and spin-down eigenfunctions.
2. For each eigenfunction, assign the proportional contribution each atom type (Cu, Fe and S) using the (normalised) squares of its orbital coefficients.
3. For each atom type, plot the EDOS as the sum of Gaussian functions, each corresponding to an eigenfunction. Each Gaussian function is centred about the eigenvalue (energy) of its corresponding eigenfunction with a height proportional to the atom type’s contribution to the eigenfunction. σ , which represents the spread of the Gaussian functions, is set to 0.6 eV.

Geometry optimisation was used to assess the accuracy of the atomic forces and the potential energy surface by comparison of the QM/MM relaxed geometry to that of the periodic QM slabs. As the MM point charges lack any short-range repulsion potential terms, the MM, QM-MM interface, and the outer part of the QM regions were kept frozen during optimisation to prevent geometric collapse onto point charges.

The final stage in the evaluation of the methodology involved the study of the adsorption of a single H₂O molecule on the CuFeS₂ surface. Geometry optimisation on both the slab and cluster systems were conducted to see whether similar adsorption geometries were obtained. In addition, potential energy surfaces of a H₂O molecule fixed in orientation relative to the surface but with varying perpendicular distances to the surface were computed under both systems and compared.

The analysis of the geometry and electronic structure was used in conjunction with the computational cost of the calculations to determine an overall cluster setup that achieves an optimal balance of accuracy and computational expense. Details of the tests conducted are detailed in the following section.

6.2.2 Test details

Cluster configuration and size

The full embedded QM/MM cluster is formed of three main components: the QM region, the MM region (consisting of point charges) and the external embedding point charges. The influence of each part of the embedded cluster on the accuracy of the QM/MM methodology was investigated by running calculations on four cluster configurations summarised in Table 6.1.

The effect of the size of the cluster was also studied. Clusters with radii of 20 (10.58), 25 (13.23), 30 (15.88), 35 (18.52) and 50 (26.46) Bohr (Å) were constructed for the $(\overline{112})$ surface. As the thickest (112)/ $(\overline{112})$ slab employed in previous periodic QM

Cluster config.	MM Point charges	Embedding charges
Bare QM	No	No
Bare QM/MM	Yes	No
Embedded QM	No	Yes
Embedded QM/MM	Yes	Yes

Table 6.1: Composition of the four different cluster configurations studied.

Label	(110) surface					$(\overline{112})$ surface				
	n_{Cu}	n_{Fe}	n_{S}	$n_{\text{Tot.}}$	Q_{net}	n_{Cu}	n_{Fe}	n_{S}	$n_{\text{Tot.}}$	Q_{net}
T1-2	1	0	3	4	-5	1	0	4	5	-7
T1-3	3	5	3	11	+12	4	6	4	14	+14
T1-4	3	5	17	25	-16	4	6	22	32	-22
T1-5	18	15	17	50	+29	19	18	22	59	+29
T1-6	18	15	53	86	-43	19	18	64	101	-55

Table 6.2: Composition of different QM regions along with the total net formal charge.

calculations in Chapter 5 was only ~ 15 Å thick, the slab was extended by duplicating the inner atomic layers to enable construction of the larger clusters.

QM region size

As the QM region is the most important component of the system, a key aim of the systematic testing was to establish a suitable size for it to achieve robust accuracy without incurring significant computational cost. The definition of the QM region was based on the coordination shells of the Cu origin using the notation described as follows. The Cu origin is referred to as the tier 1 (T1) atom. Tier 2 (T2) atoms consist of atoms in the first coordination shell of the Cu origin, equivalent to the 3-4 S atoms directly bonded to it. In general, tier n (T n) atoms consist of all the atoms in the $(n-1)$ -th coordination shell. It follows from the structure of CuFeS_2 that T n atoms only consist of S species if n is even, and only of Cu and Fe species if n is odd.

This cluster partitioning allowed the QM region to be methodically defined. The smallest QM region was defined to be T1 and T2 atoms, equivalent to the cluster origin Cu atom and the S atoms that it is bonded to. This QM region is labelled T1-2. Large QM regions were defined by incrementally including atoms from higher tiers up to T6. These QM regions are labelled T1- x , where x refers to the largest tier included in the QM region.

Table 6.2 shows the number of each atom type as well as the total formal charge of the QM regions studied for both the (110) and $(\overline{112})$ surfaces. In the initial test

	(110) surface				$(\bar{1}\bar{1}2)$ surface			
Label	n_{Cu}	n_{Fe}	n_{S}	$n_{\text{Tot.}}$	n_{Cu}	n_{Fe}	n_{S}	$n_{\text{Tot.}}$
T1-2n	3	1	3	7	2	2	4	8
T1-3n	3	5	9	17	4	6	11	21
T1-4n	10	8	17	35	11	11	22	44
T1-5n	17	15	31	63	18	18	36	72
T1-6n	25	27	53	105	32	32	64	128

Table 6.3: Composition of the new neutral QM regions, which were based on the original QM regions of Table 6.2 through addition or subtraction of atoms.

calculations of embedded clusters, the net charge of the QM region in the input was specified by summing up the formal charges of the QM atoms. However, the Mulliken charges computed not only differed significantly to the corresponding charges of the QM periodic slabs, but were also strongly incompatible with the formal charges of CuFeS_2 . It was clear that the disparity is due to the net charge of the QM region being defined using formal charges, which are significantly larger in magnitude compared to the Mulliken charges. Calculations using manually constructed neutral QM regions have therefore been performed in addition to the original calculations. The neutral QM regions were based on the original QM regions and constructed using the following principles:

1. Construction of the neutral QM region should involve adding atoms rather than removing atoms where possible.
2. New atoms should only come from the next outer tier and it is preferred to add atoms which have more bonds to the original QM region. If there are more of such atoms than needed to neutralise the charge, then those closer to the central surface Cu atom are preferred.
3. If the original net charge is positive *and* odd, the only way to achieve neutrality is to remove a (positively charged) atom as the S^{2-} anions are evenly charged. In such a scenario, remove an atom out of those with the fewest bonds to atoms in the QM region and also furthest away from the central surface Cu atom.

The neutral QM regions are labelled T1- x n, where x refers to the original QM region that the neutral QM region is based on. Table 6.3 shows the atom type composition of the neutral QM regions.

MM charge scaling

In Section 6.1.2, it was shown that by designating the MM charge magnitudes equal to the corresponding periodic QM Mulliken charges multiplied by a suitable constant scaling factor, the error in the MM electrostatic potential above the surface with respect to the QM potential is minimised. It was shown for both the (110) and ($\bar{1}\bar{1}\bar{2}$) surfaces the optimal scaling factor is ~ 0.35 . To validate this “Mulliken charge scaling” technique, a series of single point QM/MM calculations were performed for a range of scaling factors between 0.00 and 1.00, with increments of 0.05, for both surfaces.

Embedding charges

`ChemShell` parameterises the embedding charges based on the electrostatic potential generated by input reference charges. For strongly ionic materials such as ZnO, formal charges are an obvious choice for the reference charges. However, as CuFeS_2 has a mixture of ionic and covalent character, it is not so clear what reference charges should be used. An attempt was made to obtain electrostatic potential (ESP) derived atomic charges using the `REPEAT` method [238], which is developed specifically to generate ESP charges from periodic QM calculations. However, the `REPEAT` method deduced unphysical atomic charges that are drastically incompatible with both formal charges or Mulliken charges. Instead, several sets of reference charges have been tested. These included formal charges, Mulliken charges and Mulliken charges scaled by a factor of 0.35.

The effect of the number of embedding charges was also studied by altering the `ChemShell` integer parameter `bq_density`. The range of `bq_density` values trialled was all integers between 2 to 8 inclusive, corresponding to between 27 and 215 embedding point charges.

Cationic pseudopotentials in the interface region

The effect of incorporating an interface region between the QM and MM regions consisting of pseudopotentials on cationic atomic sites was investigated for the ($\bar{1}\bar{1}\bar{2}$) surface. As cations in the cluster sit in odd numbered tiers, this suggested that QM regions of $\text{T1-}x\text{n}$ should be employed, where x is even, to ensure that the interface region (of $\text{T}x+1$) lies immediately at the boundary of the QM region. A QM region of T1-4n was initially considered, but due to SCF convergence issues that could not be resolved, a QM region of T1-4 was employed instead. To avoid the introduction of excess charge into the system, the net charge of the QM region in the calculation was specified to

be the sum of the Mulliken charges, rounded to the nearest integer, instead of formal charges. The 15 Cu and 12 Fe atoms of T5 formed the interface region, which were represented by LANL pseudopotentials [182].

Geometry optimisation

A range of QM regions were employed in geometry optimisations of the QM/MM surface clusters. As with the QM regions, the active region was defined methodically based on the coordination shells surrounding the Cu origin and are labelled the same way using the T1- x notation. For each QM region size a range of active region sizes were considered. The smallest active region was only T1, and the largest consisted of all tiers up to the tier immediately inside the maximum tier of the QM region. For example, the active regions considered when the QM regions was T1-4n were T1, T1-2 and T1-3. As explained previously, this prevents collapse of atoms onto the MM point charges due to the neglect of short-range repulsion terms in the MM region.

H₂O adsorption

The final phase of the QM/MM methodology testing involved study of the adsorption of a single H₂O molecule on the (110) and $(\overline{1}\overline{1}2)$ surfaces. In the first test, geometry optimisation of H₂O on the surface was performed for both the slab and cluster systems and the adsorption energy and relaxed geometry were computed. As reported in the following section, the optimised geometry of the cluster surface is clearly unphysical and hence the optimised slab geometry was used and kept frozen during relaxation. This not only prevented collapse of the surface structure in the cluster system but also ensured that a like-for-like comparison could be made between cluster and slab systems.

In the second test the potential energy surface was computed for a fixed H₂O orientation relative to the surface except with varying perpendicular distance to the surface. The H₂O molecule was oriented such that the O atom was situated directly above the cluster origin Cu and below the two H atoms which were in the same x - y plane and aligned along y -axis. The distance between Cu and O was varied between 1.6 and 7 Å.

6.2.3 Computational details

All QM/MM calculations were performed using the **ChemShell** code, which provides a computational shell environment for QM/MM simulations via its interface with a wide range of QM and MM computational packages [167,168]. Geometry optimisation is performed by the DL-FIND optimiser library [239] which is distributed as part of

ChemShell. To allow suitable comparison between slab and cluster calculations, the same exchange-correlation functional (B3LYP) and triple-valence basis sets employed in the QM calculations of CuFeS₂ bulk (Chapter 4) and slabs (Chapter 5) were employed here. As **ChemShell** does not have an interface with the **CRYSTAL** code, **Gaussian09** was used as the QM code [240]. The inbuilt `construct_cluster` command was used to generate the embedded clusters. Unless specified, the clusters employed have a radius of 25 Bohr, a QM region size of T1-5n, a MM charge scaling factor of 0.35 and a `bq_density` of 5. In addition, the default setup does not include an interface region.

To estimate the random error in the computed Mulliken charges, sets of 10 single point calculations were performed for each QM region size with the default cluster setup. The Mulliken charges of cluster and slab systems were compared by calculating the RMS error between charges of corresponding atoms. To ensure reasonable comparison between clusters with different QM regions, the RMS error was calculated for each tier of atoms. As it is more important to correctly describe the electronic structure of the inner QM region close to the active site, the EDOS of clusters was projected onto T1-3 atoms while the DOS of slabs was projected onto atoms of the outermost repeating unit.

6.3 Test results of the QM/MM methodology

6.3.1 Cluster configuration and size

Figure 6.11b, shows the RMS error in the Mulliken charges of the four cluster configurations in Table 6.1. As expected, the RMS error is generally higher for outer tiers as the atoms in such tiers are closer to the MM region. The RMS error of the outermost part of the QM region (T5) is lower for QM/MM clusters compared to QM clusters by around 0.09 and 0.07e for the (110) and $\overline{(112)}$ surfaces respectively. For other parts of the QM region, the effect due to MM charges is either far less positive, or for the case most inner tiers (T1 and T2), is even detrimental. The inclusion of embedding charges results in negligible change to the Mulliken charges throughout the whole QM region.

The EDOS of the bare QM and embedded QM/MM clusters are compared with the surface DOS of the corresponding slab for the (110) and $\overline{(112)}$ surfaces in Figures 6.12a and 6.12b respectively. In general, the cluster EDOS share the same broad features with the slab DOS for both surfaces, though several differences can be observed. First, the cluster systems predict band gaps smaller by ~ 0.5 eV compared to corresponding slab systems. This is partially accounted for by the Gaussian spread applied to the

cluster eigenvalues to produce the EDOS. Second, the occupied Fe band in the cluster EDOS is centred at a lower energy and has a much larger bandwidth compared to the slab counterpart. Comparing cluster configurations, the EDOS of bare QM cluster closely resembles that of the embedded QM/MM cluster. This is consistent with the similarity in the computed Mulliken charges in the inner QM region for the two cluster configurations.

There is no discernible difference in the computational cost in terms of CPU time per SCF cycle for the different cluster configurations. This is because the QM calculations account for the vast majority ($\sim 99\%$) of the total computational time.

Figure 6.13 plots the RMS error in the cluster Mulliken charges for individual QM region tiers as a function of the cluster radius. The data shows that increasing the cluster radius does not systematically improve the accuracy of the Mulliken charges. It is therefore concluded that the error arising from having a small cluster is not a main contributing error in this methodology. In addition, for a given QM region size, the computational cost in terms of CPU time per SCF cycle was essentially constant over all cluster radii. This is expected as the QM region is constant.

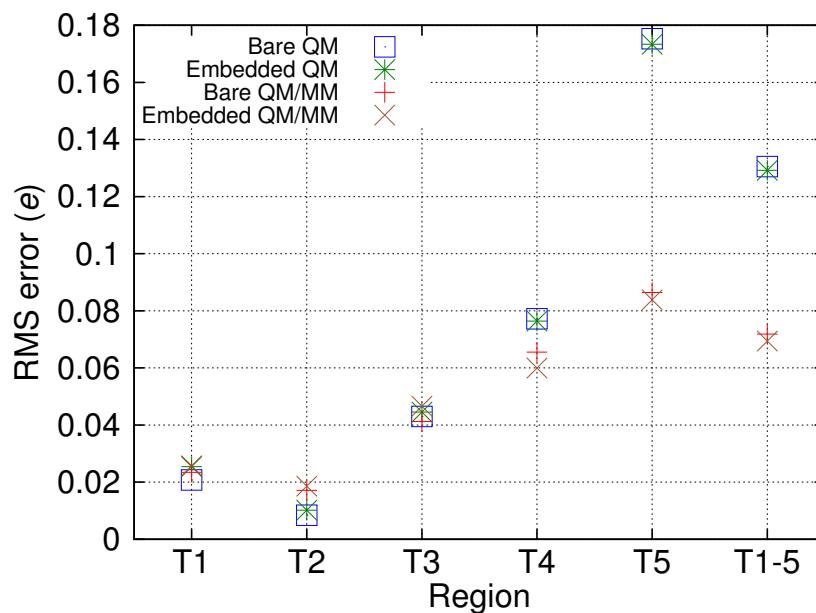
6.3.2 QM region size

As discussed in Section 6.2, the use of non-neutral QM regions resulted in large disparities between cluster and slab Mulliken charges, leading to the adoption of neutral QM regions. This is illustrated in Figure 6.14a, which shows the RMS error of the Mulliken charges for the (110) clusters with different QM regions, and Figure 6.14b, for the $(\bar{1}\bar{1}\bar{2})$ clusters. It is clearly seen that for QM regions of similar sizes, clusters with neutral QM regions have errors that are lower, and often significantly so, compared to clusters with non-neutral regions. For example, for $(\bar{1}\bar{1}\bar{2})$ cluster with QM regions T1-2 and T1-3, the RMS error relative to the cluster with QM region T1-2n is larger by approximately $1.1 e$ and $0.2 e$ respectively. Calculations with non-neutral QM regions, apart from the those for the investigation of the interface region, are therefore henceforth disregarded from discussion.

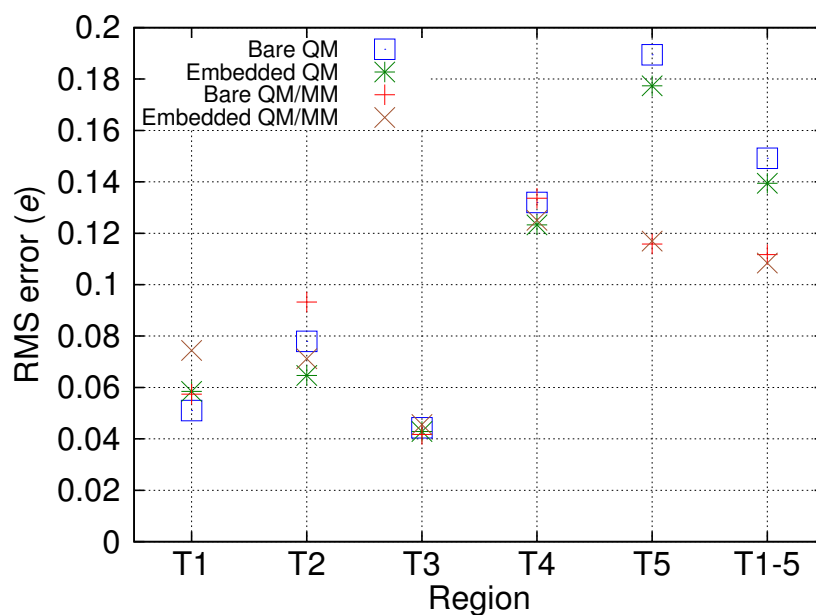
To ease analysis, the data in Figures 6.14a and 6.14b has been replotted in Figures 6.15a and 6.15a but with that corresponding to non-neutral QM regions removed. The following conclusions can be drawn:

1. Generally, the larger the QM region, the smaller the errors. In addition, gradual convergence of the cluster Mulliken charges to those of the periodic system with increasing QM region size is observed. However, for the largest QM region size

Figure 6.11: RMS errors in the Mulliken charges for different cluster configurations.

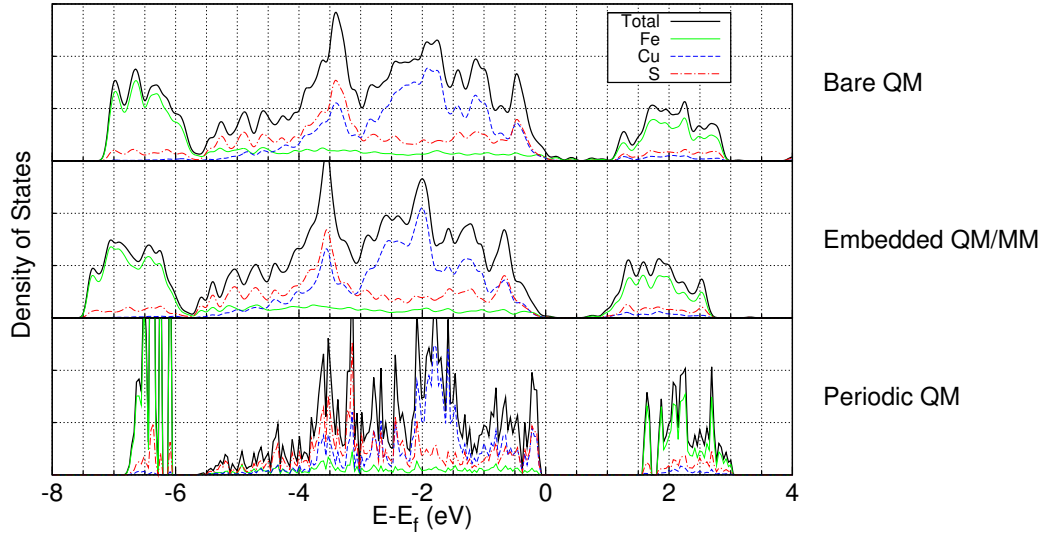


(a) Plot for the (110) surface.

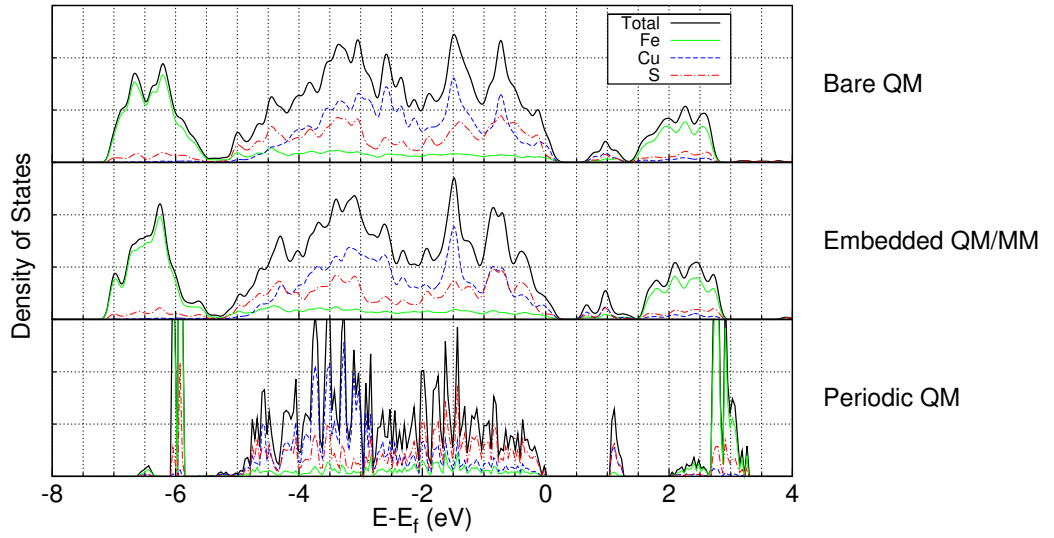


(b) Plot for the (112) surface.

Figure 6.12: Plots of the EDOS for the bare QM and embedded QM/MM cluster configurations. The slab DOS is shown for reference.



(a) Plot for the (110) surface.



(b) Plot for the $(\overline{112})$ surface.

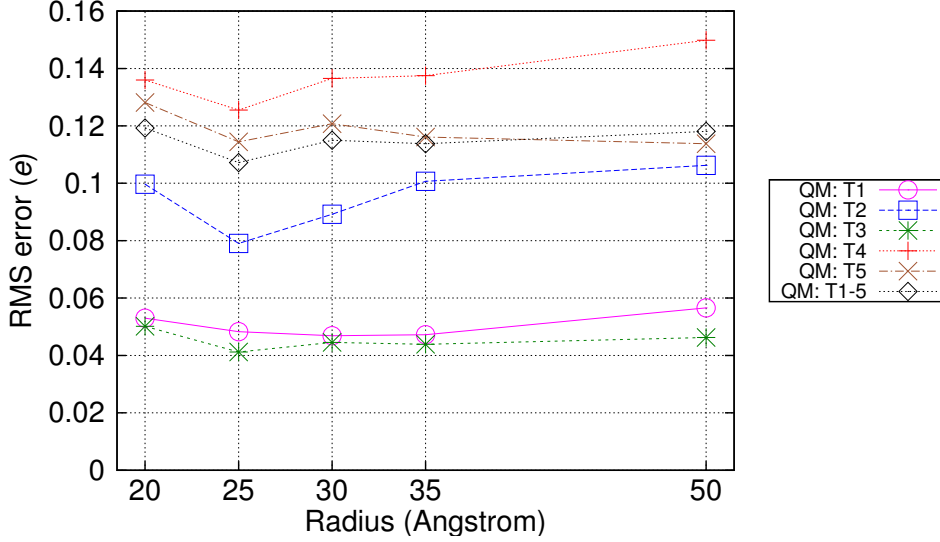


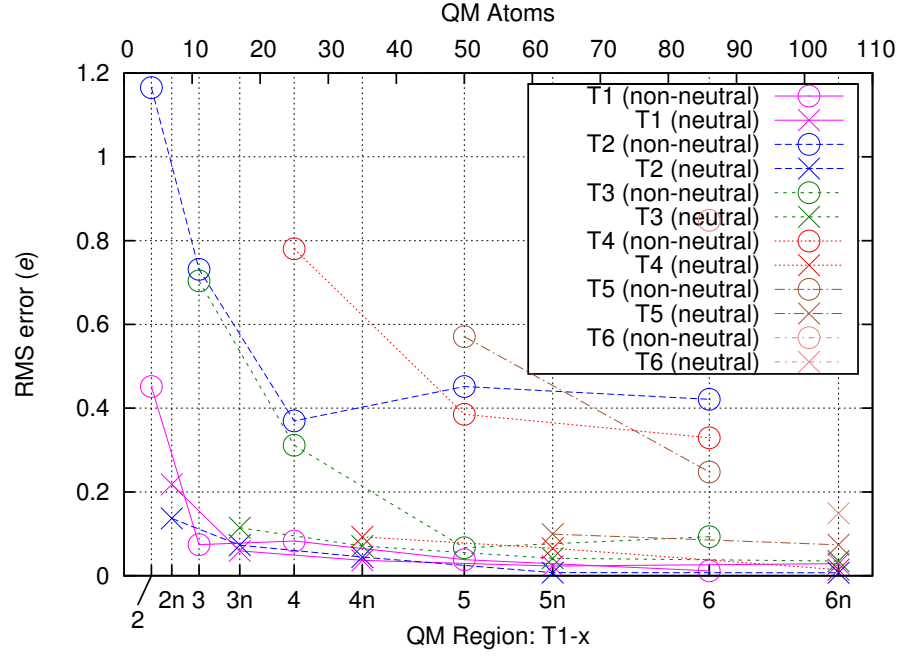
Figure 6.13: RMS errors in the $(\bar{1}\bar{1}\bar{2})$ Mulliken charges for different cluster radii.

(T1-6n), there remains a RMS error of around of $\sim 0.05e$ in the inner tiers of the QM region.

2. For a given QM region size, the RMS error is much larger for outer tiers compared to inner tiers. This provides further confirmation that the MM point charges significantly impact the electronic structure of nearby QM atoms, but has a limited long-range effect.
3. The similar error magnitudes and trends exhibited by both surfaces confirms that the embedded finite cluster methodology can be equally applied to both non-polar and polar surfaces.

Figure 6.16a plots the EDOS of the (110) clusters with QM regions between T1-3n and T1-6n as well as the corresponding slab DOS. The same is plotted in Figure 6.16b but for the $(\bar{1}\bar{1}\bar{2})$ surface. It can be seen for both surfaces, that the widths and energies of the main valence band, which mainly consists of $3d$ -Cu and $3p$ -S states, shows convergence to those of the slab with increasing QM region size. The centre of the lower $3d$ -Fe valance band also converges to that of the slab, but in general the band dispersion is considerably larger. The cluster band gap approaches the slab counterpart for the (110) surface with with increasing QM region size. However, this is not the case for $(\bar{1}\bar{1}\bar{2})$; the band gap is underestimated by 0.5 eV for cluster with the largest QM region.

Figure 6.14: RMS errors of the Mulliken charges for all QM region sizes.



(a) Plot for the (110) surface.

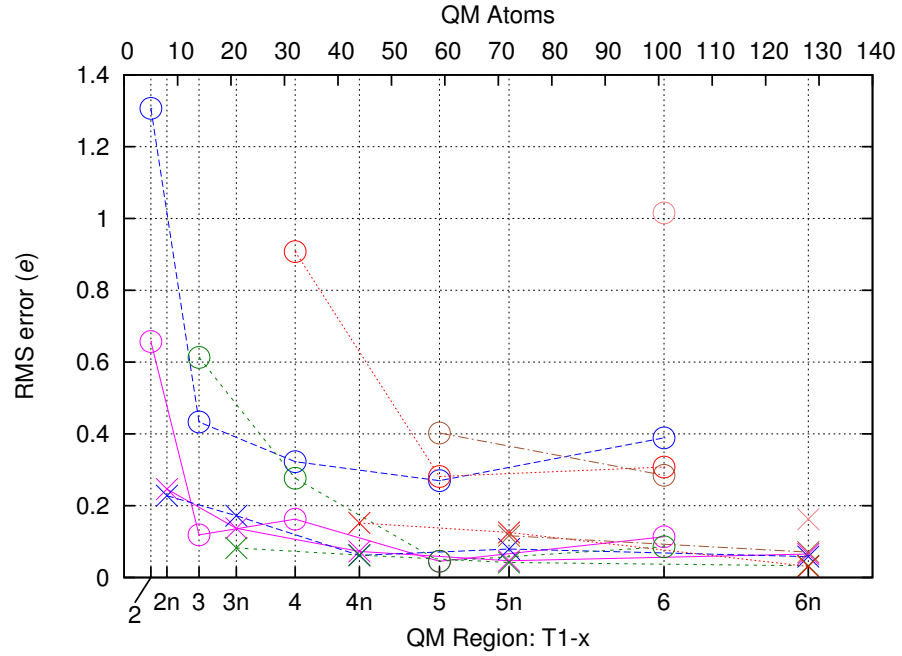
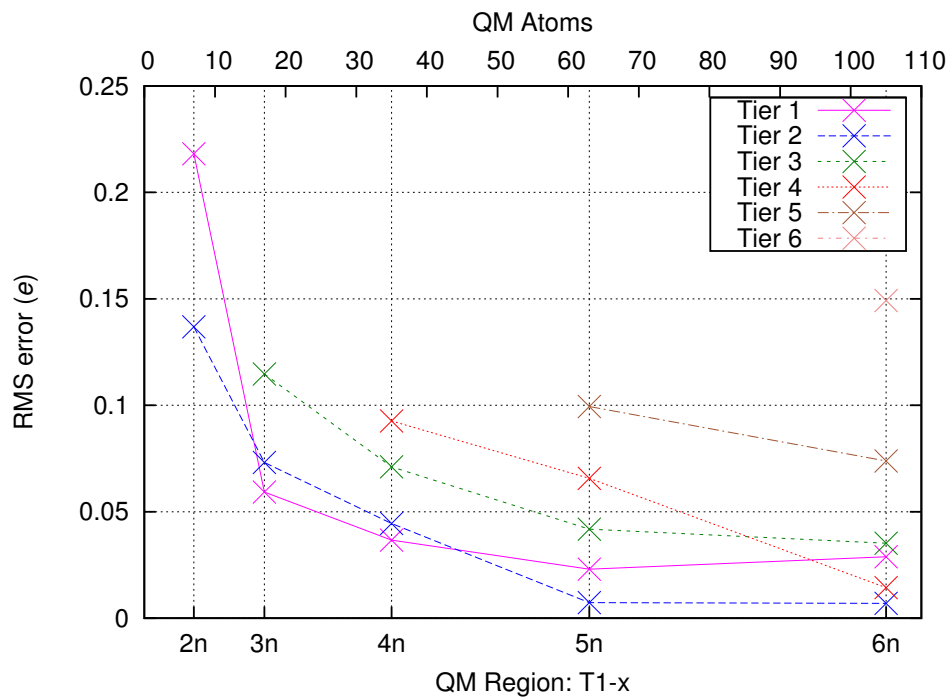

 (b) Plot for the $(\bar{1}\bar{1}2)$ surface.

Figure 6.15: Same as Figure 6.14 but for clusters with neutral QM regions only.



(a) Plot for the (110) surface.

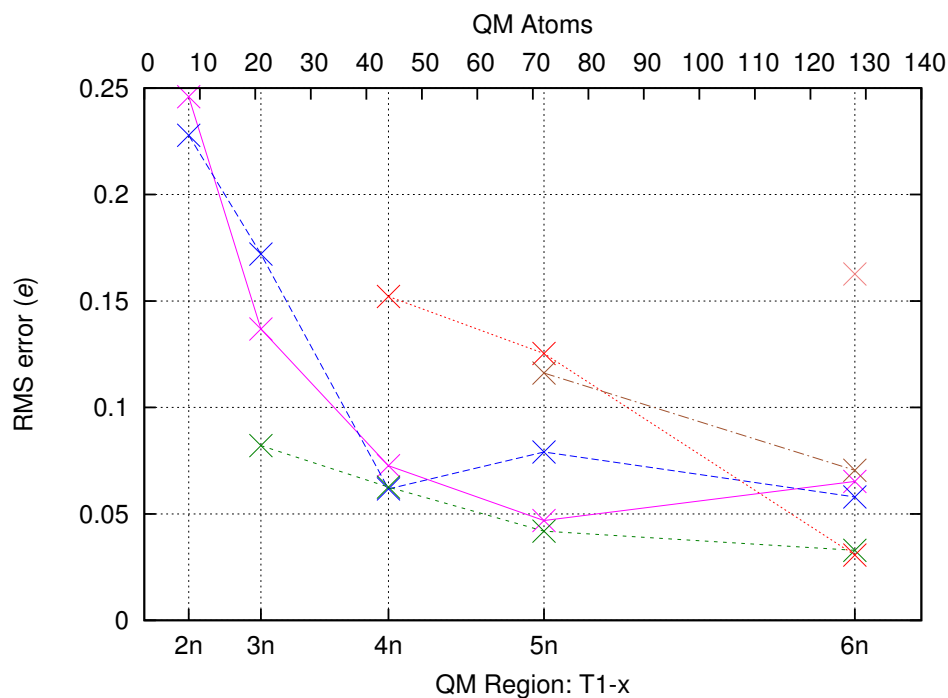
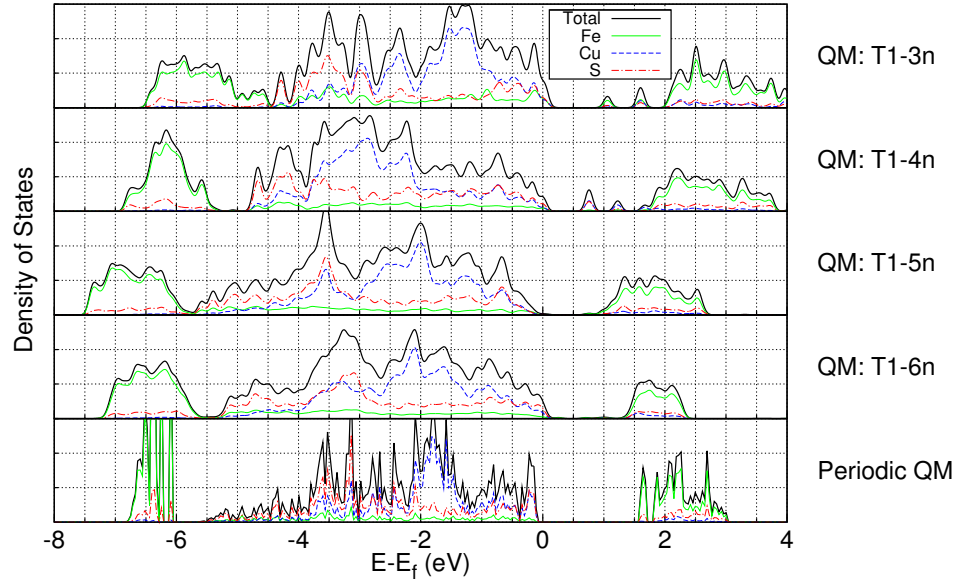
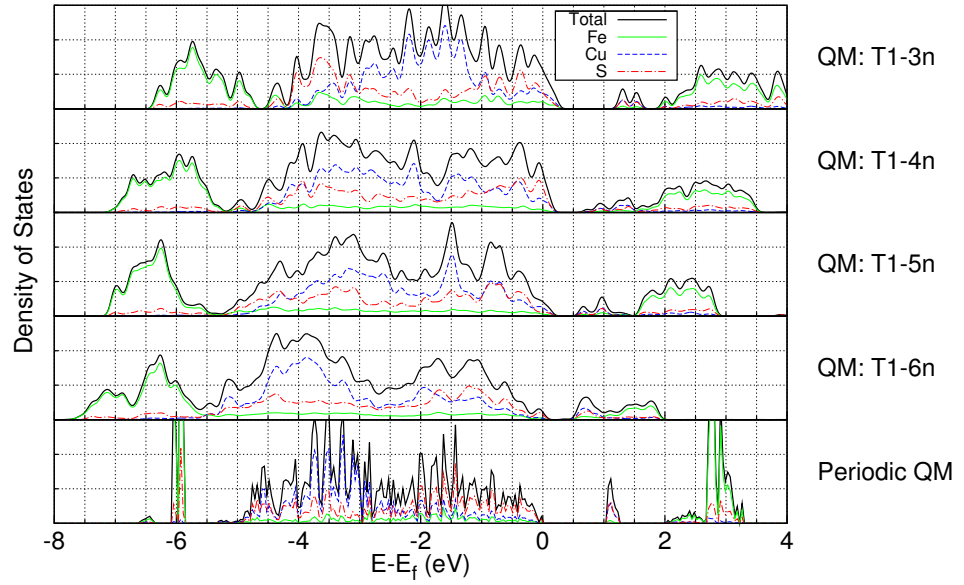
(b) Plot for the $(\bar{1}\bar{1}2)$ surface.

Figure 6.16: Plots of cluster EDOS for different sizes of neutral QM regions. The slab DOS is shown for reference.



(a) Plot for the (110) surface.



(b) Plot for the $(\bar{1}\bar{1}2)$ surface.

QM region size	QM atoms	Wall time (hours)
T1-2n	8	0.01
T1-3n	21	0.16
T1-4n	44	1.56
T1-5n	72	5.81
T1-6n	128	22.04

Table 6.4: Comparison for the computational cost of a single point calculation of the embedded QM/MM ($\overline{112}$) cluster for various QM region sizes.

The total computational expense associated with single point calculations of the QM/MM embedded clusters is essentially the product of the computational cost of a single SCF cycle with the number of SCF cycles required for convergence of the wavefunction in the QM calculation. Figure 6.17 plots these two factors as a function of the number of QM atoms for the ($\overline{112}$) clusters. It is clear from the figure, that the total computational cost is mainly governed by the average computational cost of an SCF cycle. Further analysis has established that the average CPU time per SCF cycle is roughly proportional to the number of QM atoms to the power of 2.37. Figure 6.17 also shows that the larger QM regions generally require more SCF cycles for convergence than smaller QM regions. This adds further to the total computational cost for clusters with large QM regions. Table 6.4 shows the average total wall time required for a single point calculation on the ($\overline{112}$) surface using 20 cores, the maximum number on a single node, on the Imperial high performance computing platform `cx1` for all neutral QM region sizes.

The data presented shows that enlarging the QM region beyond a size of T1-4n results in negligible improvement in the accuracy of the electronic structure within the inner part of the QM region while incurring a heavy increase in the computational cost. Compared to a QM region size of T1-4n, T1-5n gives a RMS error in the Mulliken charges of T1-3 only 0.008e lower while incurring an average computational time that is 3.7 times longer. The corresponding numbers for a QM region size of T1-6n, is 0.019 e and 14.1 times. This is supported by the EDOS analysis, in which no systematic improvement in reproducing the slab DOS was observed for clusters with large QM regions. A QM region of T1-4n, which consists of 35 and 44 atoms for (110) and ($\overline{112}$) respectively, is larger than the size of typical QM regions used in previous finite embedded clusters studies of surfaces listed in Table 3.2. Within the range of QM region sizes studied, the computational cost is not a prohibitive factor for a single point calculation. However, for other types of calculations such as geometry optimisations or

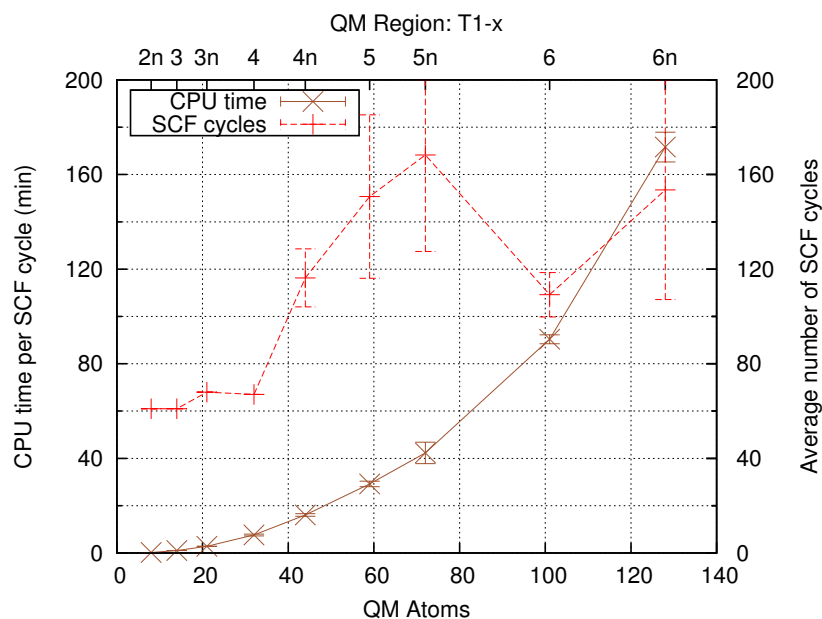


Figure 6.17: Plot of average CPU time and SCF cycles required for convergence in single point calculations of embedded QM/MM ($\bar{1}\bar{1}\bar{2}$) clusters for various QM region sizes.

nudged elastic band studies where a large number of single point evaluations may be required, the QM region size needs to be carefully considered.

6.3.3 MM charge scaling factor

Figure 6.18a plots the RMS error in the cluster Mulliken charges of each tier for the (110) surface for scaling factors between 0.00 and 1.00. The same is plotted in Figure 6.18b, but for the ($\bar{1}\bar{1}\bar{2}$) surface. For both surfaces, the lowest RMS error for the outermost tier (T5) is obtained when the scaling factor is 0.4. This is consistent with the optimal scaling factor of 0.35 predicted in Section 6.1.2 and hence provides validation of the process, based on reproducing the electrostatic potential, devised to determine the optimal scaling factor. However, the influence of the charge scaling factor on the Mulliken charges is limited, not just in scope (to the outermost QM atoms), but also in magnitude. Compared to a scaling factor of 1, which gives the least accurate T5 Mulliken charges, the improvement in the RMS error for scaling factor of 0.40 is 0.12 and 0.08e for (110) and ($\bar{1}\bar{1}\bar{2}$) respectively. For the inner parts of the QM region, there is no systematic improvement in the Mulliken charges as the scaling factor approaches 0.4. Intriguingly, for the ($\bar{1}\bar{1}\bar{2}$) surface, the RMS error for T2 atoms gradually increases

Embedding reference	RMS Error (e)					
	T1	T2	T3	T4	T5	T1-3
Formal charges	0.040	0.040	0.034	0.094	0.203	0.036
Mulliken charges	0.047	0.079	0.042	0.125	0.116	0.055
Scaled Mulliken charges	0.066	0.078	0.044	0.133	0.119	0.058
No embedding	0.039	0.097	0.042	0.130	0.120	0.063

Table 6.5: RMS errors of $(\bar{1}\bar{1}\bar{2})$ Mulliken charges for different reference charges used to parameterise the embedding charges.

with scaling factor. For other tiers, there is either a weak or no clear trend in the RMS error with respect to the scaling factor.

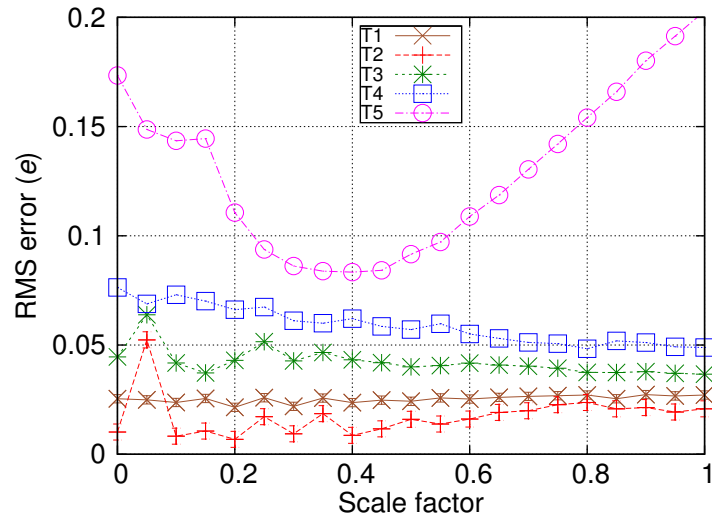
Figure 6.19a plots the EDOS of the (110) surface cluster for scaling factors of 0.00 (bare QM/MM cluster), 0.35 and 1.00 in addition to the surface DOS of the slab. The same is plotted in Figure 6.19b, but for the $(\bar{1}\bar{1}\bar{2})$ surface. For both surfaces, there is no indication that the EDOS computed using the optimal scaling factor (0.35) more closely represents the slab DOS compared to other scaling factors. As the EDOS are only projected on T1-3 atoms, this is consistent with the trends observed in the computed cluster Mulliken charges.

6.3.4 Embedding charges

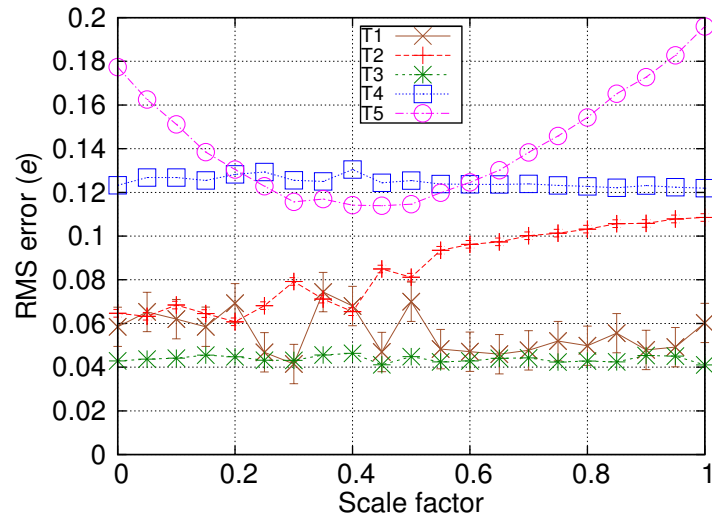
Reference charges for parameterisation. Table 6.5 shows the tier by tier RMS error of the cluster Mulliken charges as well as the RMS error of the inner (T1-3) QM region for the different reference charges used to parameterise the embedding charges. Systematic, albeit minor, improvement of T1-3 charges is observed as the reference charges approach the formal charges. This suggests that out of all reference charges considered, formal charges result in the best description of the electrostatic potential within the surface, which in turns implies that interatomic interactions are mostly ionic. This is in spite of the fact that Cu-S interactions in CuFeS_2 were deduced in Chapter 4 to have considerable covalent character. On the contrary, the use of formal charges as reference for embedding gives rise to the largest RMS error in the T5 Mulliken charges by a significant margin ($\sim 0.08e$). This may be due to the interplay of the relatively large electrostatic field at the QM region boundary due to the embedding charges with nearby MM point charges leading to substantial interatomic charge transfer at the boundary of the QM region.

Number of embedding charges. Figure 6.20 plots the RMS error of the Mulliken charges in different QM region tiers as a function of the parameter `bq_density`. The

Figure 6.18: RMS errors of Mulliken charges for different Mulliken charge scaling factors.

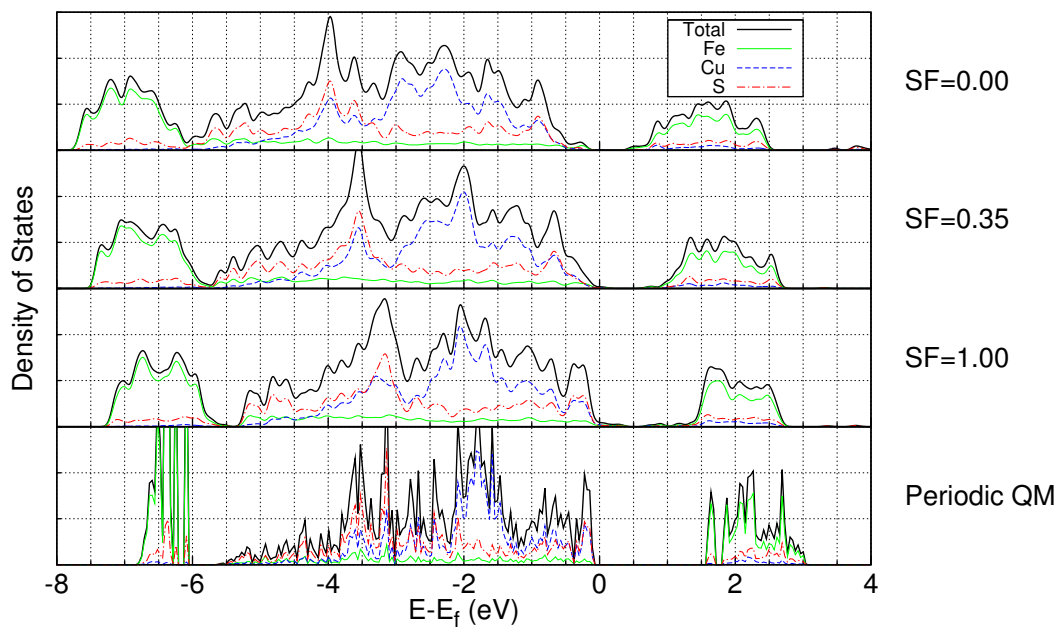


(a) Plot for the (110) surface.

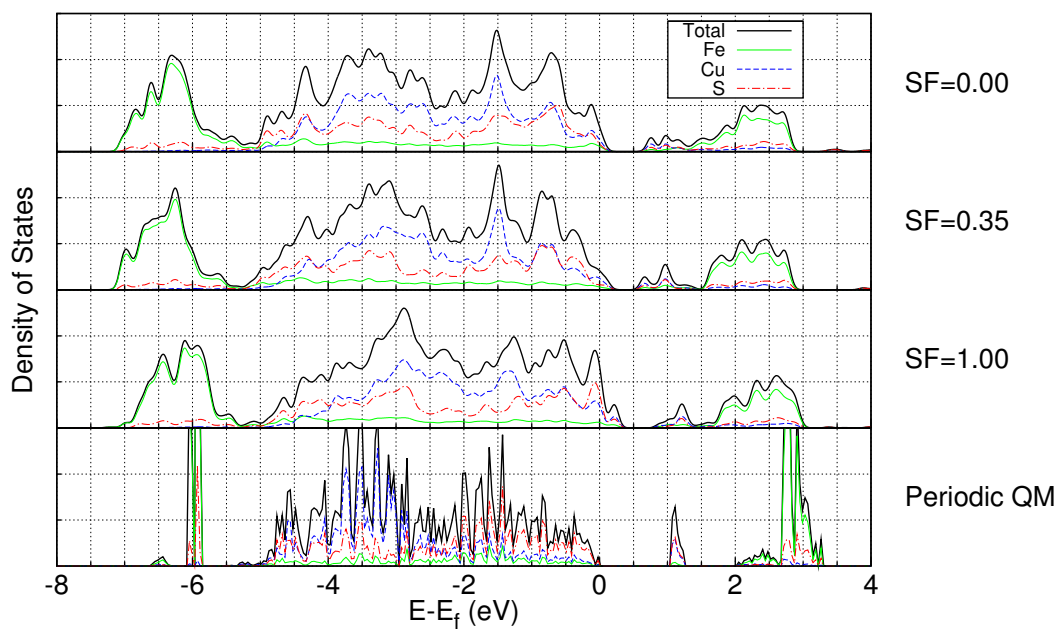


(b) Plot for the $(\bar{1}\bar{1}2)$ surface.

Figure 6.19: Comparison of the cluster EDOS for selected Mulliken charge scaling factors. The slab DOS is shown for reference.



(a) Plot for the (110) surface.



(b) Plot for the $(\bar{1}\bar{1}2)$ surface.

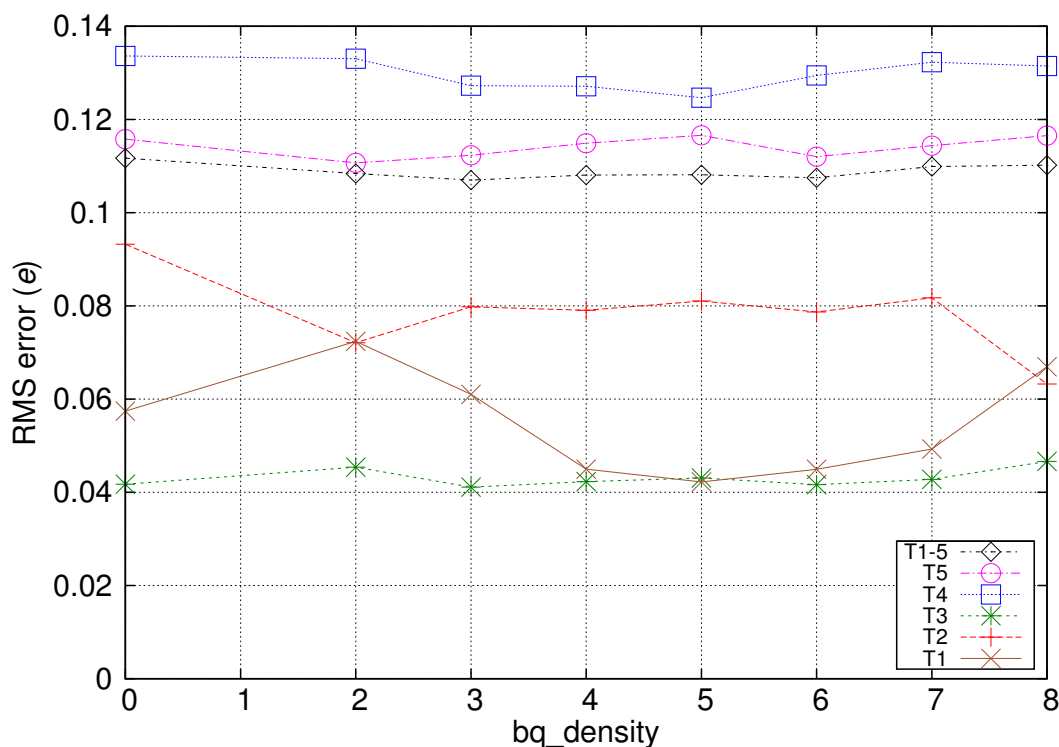


Figure 6.20: RMS error of $(\overline{112})$ Mulliken charges for different `bq_density` values.

figure shows that the number of embedding charges has little effect on the accuracy of the resulting Mulliken charges. Furthermore, there is no systematic improvement observed as the number of embedding charges is increased. This is consistent with the earlier observation that the Mulliken charges of embedded clusters are not significantly more accurate than those of the bare clusters relative to the periodic QM counterparts.

6.3.5 Interface region

Table 6.6 shows the RMS errors in the Mulliken charges for $(\overline{112})$ clusters with and without an interface region. The data shows that the RMS errors of T1 and T3 Mulliken charges are considerably lower, by $0.05e$ and $0.07e$ respectively, when the interface region is included. In contrast, the RMS error of T2 and T4 Mulliken charges are higher, albeit by a smaller magnitude. There is little difference in the EDOS of the two clusters, as shown in Figure 6.21. It is therefore concluded that the inclusion of an interface region in the QM/MM cluster has at best a marginal beneficial effect on the

Setup	RMS Error (e)			
	T1	T2	T3	T4
With interface	0.010	0.071	0.015	0.123
Without interface	0.061	0.032	0.085	0.105

Table 6.6: Comparison of the RMS error of Mulliken charges for embedded QM/MM $(\bar{1}\bar{1}\bar{2})$ clusters with and without an interface region.

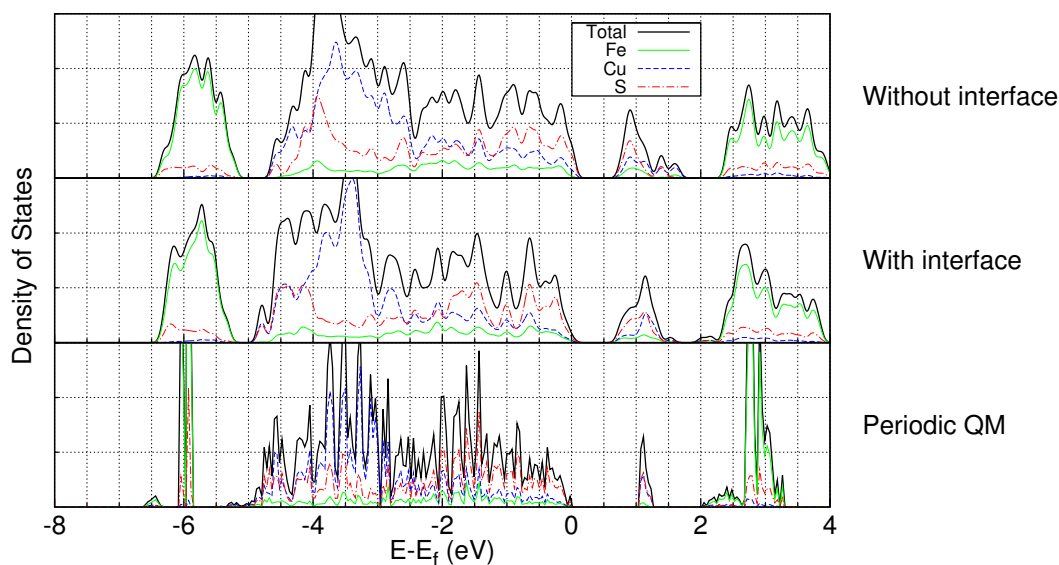


Figure 6.21: EDOS of the embedded $(\bar{1}\bar{1}\bar{2})$ clusters with and without an interface region. The slab DOS is shown for reference.

accuracy of the electronic structure.

6.3.6 Geometry optimisation

Overall, atomic forces, and hence the relaxed geometric structure, is poorly described by the methodology. Table 6.7 shows the average absolute change in the bond lengths during relaxation, for both surfaces. The relaxation energy, which is the difference in energy between the initial (slab) and relaxed geometry, is also shown. Even with small active region sizes, there was significant distortion of bonds during relaxation. For a constant QM region, the degree of distortion generally increased with larger active region, and is reflected by the significant increase in relaxation energy.

Figure 6.22 compares the initial geometry with the relaxed geometry of clusters with a QM region of T1-4n and an active region of T1-3 for the (110) surface. The same

QM/MM setup		$\overline{\Delta x}$ (Å)			E _{Relax} (eV)
QM Region	Active Region	T1-T2	T2-T3	T3-T4	
(110) surface					
T1-2n	T1	0.043	N/A	N/A	0.01
T1-3n	T1	0.635	N/A	N/A	0.9
	T1-2	0.554	0.428	N/A	8.9
T1-4n	T1	0.749	N/A	N/A	2.5
	T1-2	0.186	0.377	N/A	11.9
	T1-3	0.183	0.439	0.457	22.2
T1-5n	T1	0.749	N/A	N/A	1.8
	T1-2	0.636	0.223	N/A	16.0
	T1-3	0.267	0.486	0.276	24.0
(112) surface					
T1-2n	T1	0.325	N/A	N/A	0.3
T1-3n	T1	0.698	N/A	N/A	0.9
	T1-2	0.443	0.286	N/A	11.8
T1-4n	T1	0.142	N/A	N/A	0.5
	T1-2	0.306	0.380	N/A	16.3
	T1-3	0.620	0.704	0.393	29.3
T1-5n	T1	0.241	N/A	N/A	0.9
	T1-2	0.246	0.256	N/A	16.1
	T1-3	0.288	0.759	0.307	28.7

Table 6.7: Absolute difference $|\overline{\Delta x} \text{ (\AA)}|$ between cluster and slab models of average bond lengths of the optimised geometry. The relaxation energy of the surface is also shown.

is shown in Figure 6.23, but for the $(\overline{112})$ surface. It is seen from the figures that relaxation of the cluster system resulted in general collapse of the active atoms into the surface resulting in complete loss of the original ordered surface coordination structure. This is supported by the computed relaxation energies. For the largest active region, the magnitude of the relaxation energies (20-30 eV) indicate that the initial geometry of the cluster system is extremely unstable.

6.3.7 H₂O adsorption

Optimisations of a H₂O molecule on the surface show that vastly different adsorption behaviour of H₂O is predicted by the finite embedded cluster methodology compared to the QM slab model. In the slab system, very weak binding of H₂O to both the (110) and $(\overline{112})$ surfaces is observed, with calculated adsorption energies of ~ 0.1 eV. On the

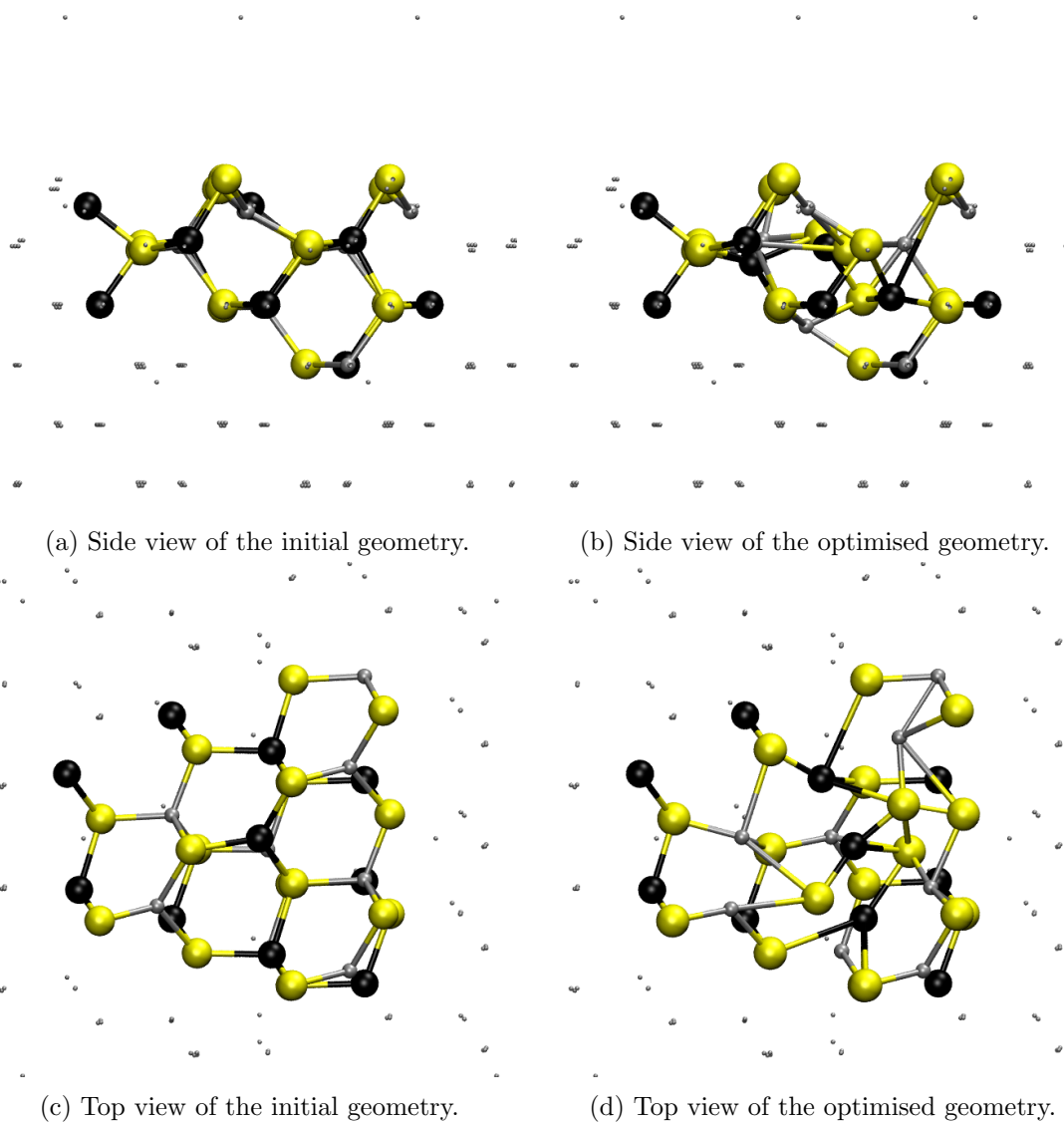


Figure 6.22: The initial and optimised geometries of the (110) cluster surface. Note that the initial geometry corresponds to the optimised (110) periodic slab geometry. The copper, iron and sulphur atoms are coloured black, silver and yellow respectively.

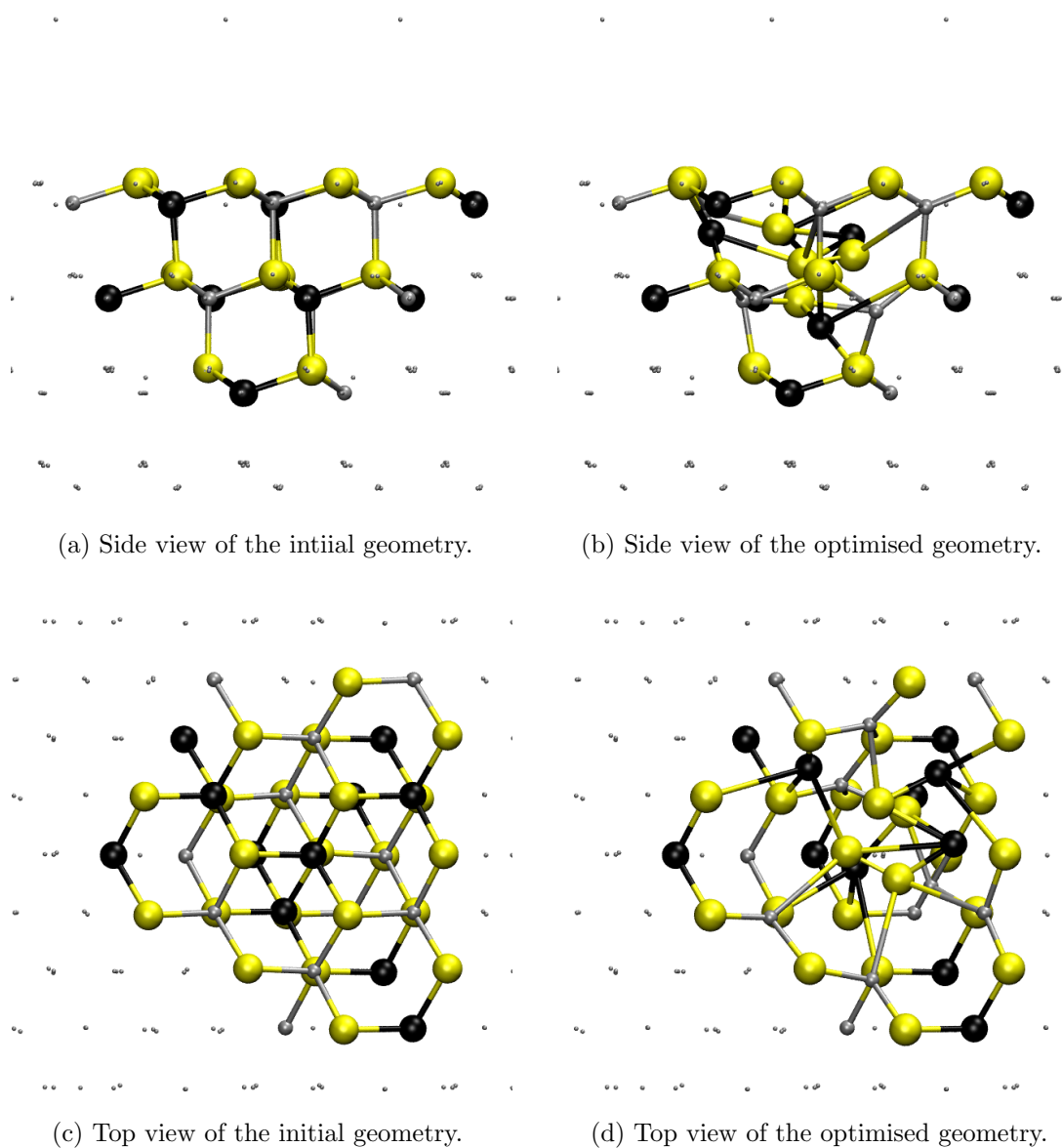


Figure 6.23: Same as Figure 6.22 but for the $(\bar{1}\bar{1}2)$ cluster.

contrary, strong binding is observed in the cluster system, with absorption energies of ~ 6 eV and ~ 3 eV for the (110) and the $(\bar{1}\bar{1}\bar{2})$ surfaces respectively. Figures 6.25a and 6.25b show the final optimised geometry of the adsorbed H_2O for the slab and cluster systems respectively for the $(\bar{1}\bar{1}\bar{2})$ surface. The figures show that the slab and cluster models also predict different orientations of the adsorbed H_2O relative to the surface.

To check whether the different adsorption behaviour predicted was as a result of the systems reaching different local minima of the potential energy surface, the optimisations were re-run on each system except starting with optimised geometry of adsorbed H_2O from the other system. However, the systems relaxed back to the predicted geometry of the initial calculations.

The potential energy surfaces for fixed H_2O orientation compliment the results above. Figure 6.26 shows the binding energy of H_2O on $(\bar{1}\bar{1}\bar{2})$ as a function of Cu-O distance computed on the slab model as well as the cluster model with varying QM region sizes. The figure shows the contrast in the binding behaviour between slab and cluster model, with weak binding exhibited on the slab and strong binding on the cluster. The binding energy and the Cu-O distance of the minima are similar with slight variation across the clusters with different QM regions. There is no systematic shift of the binding energy towards that of the QM slab system with increasing QM region size.

In addition to the data presented, it was also observed that the neither the inclusion of an interface region nor the use of different reference embedding charges (formal and scaled Mulliken) results in notable improvement of the potential energy surface. As mentioned above, the reason for the discrepancy between the slab and cluster models may be attributed to the lack of self-consistent polarisation between QM and MM regions, in addition to the inaccurate electrostatic potential due to poorly parameterised embedding charges.

6.3.8 Critical assessment of the methodology

The tests conducted show that the most important element of the finite embedded cluster methodology for a reliable description of the electronic structure is the size of the QM region. Convergence of the Mulliken charges to the slab counterparts was observed with increasing size of the QM region for both (110) and $(\bar{1}\bar{1}\bar{2})$. With a QM region of T1-4n or larger, corresponding to around 40 atoms or more, the cluster Mulliken charges of the inner QM regions (T1-3) have an RMS error relative to the slab counterparts

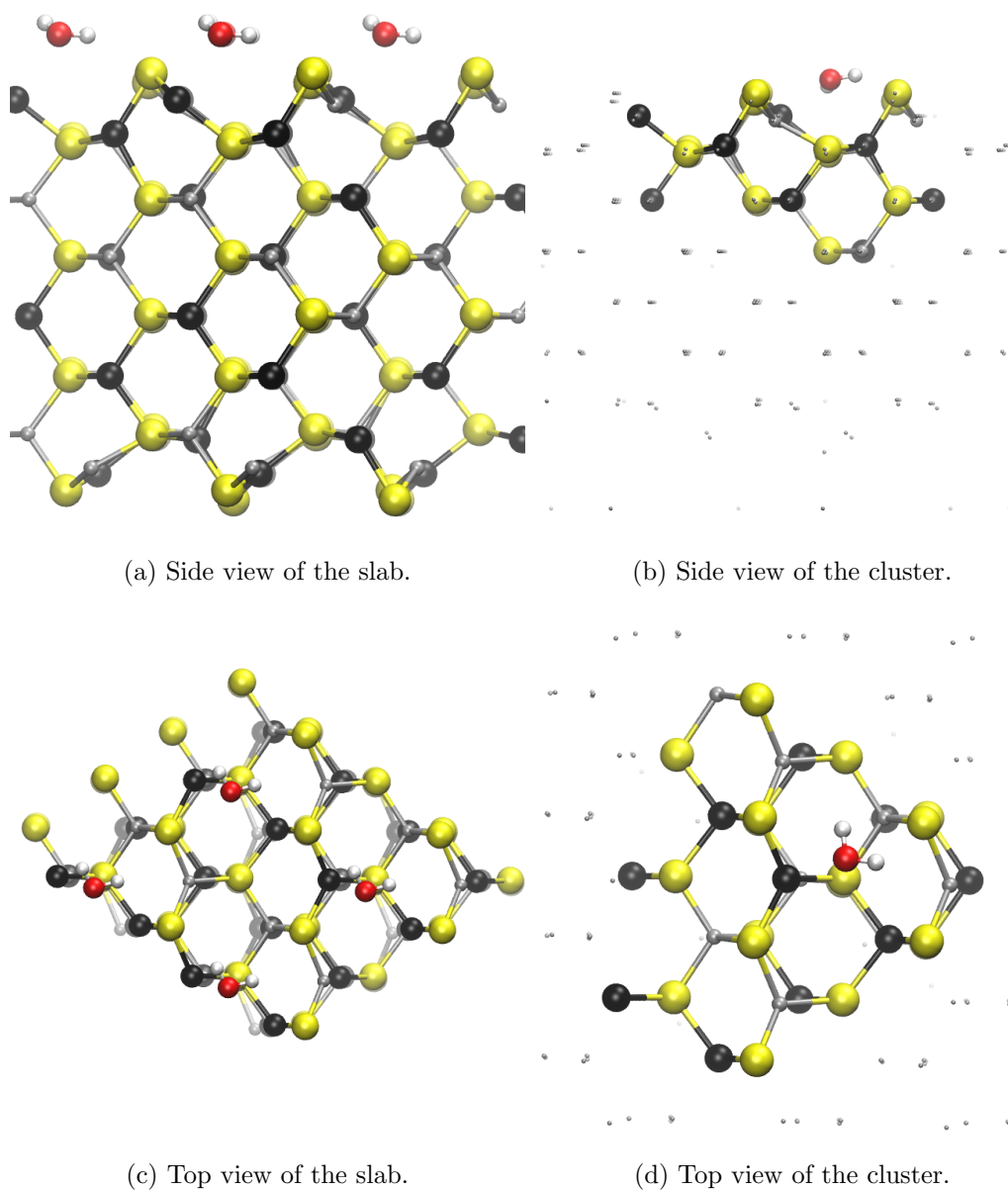


Figure 6.24: Optimised geometry of an adsorbed H_2O molecule on the (110) surface under the periodic slab and embedded cluster approaches. For the slab, the 2×2 super-cell is shown. Copper, iron, sulphur, oxygen and hydrogen atoms are coloured black, silver, yellow, red and white respectively.

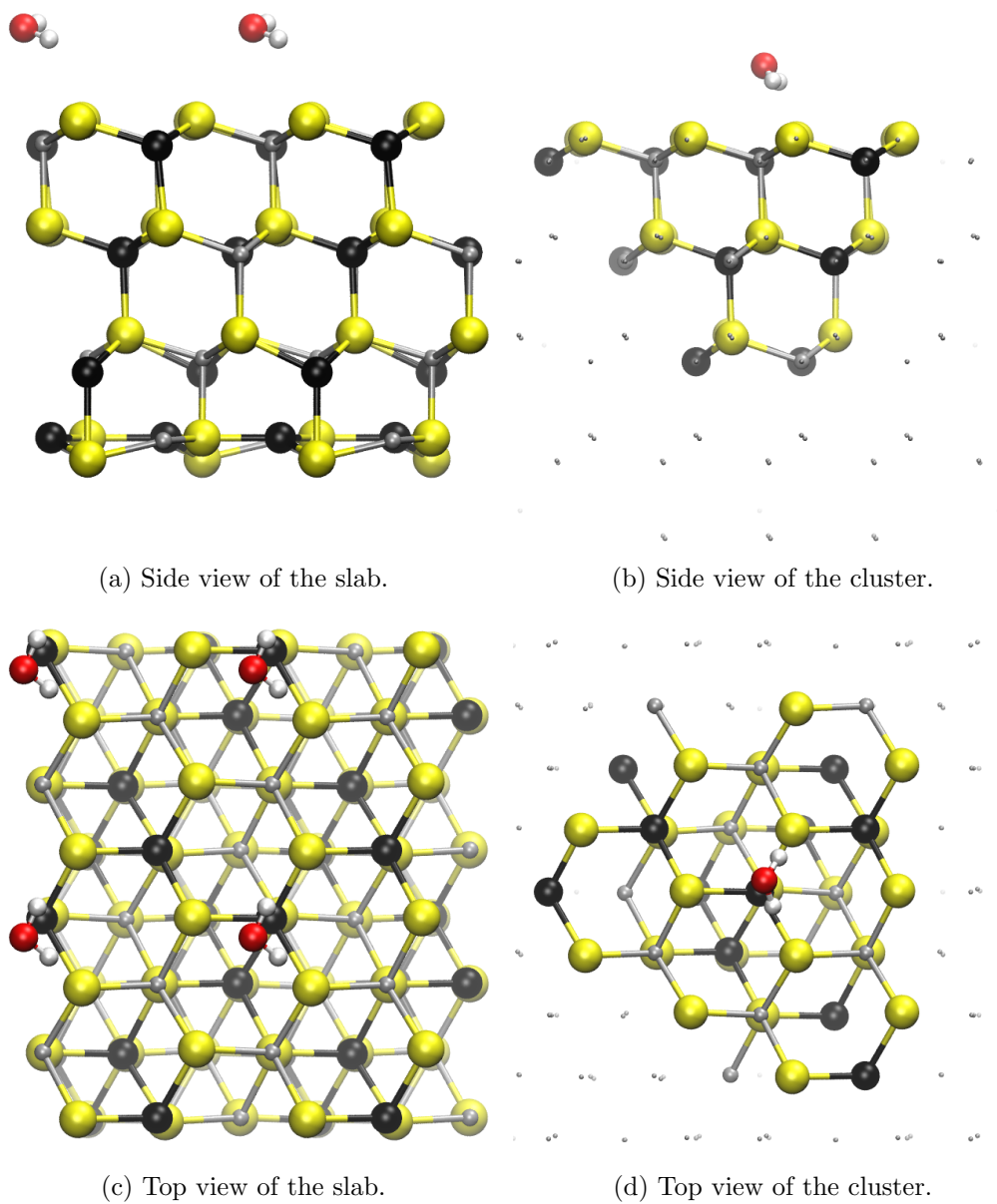


Figure 6.25: Same as Figure 6.24 but for the $(\overline{112})$ surface.

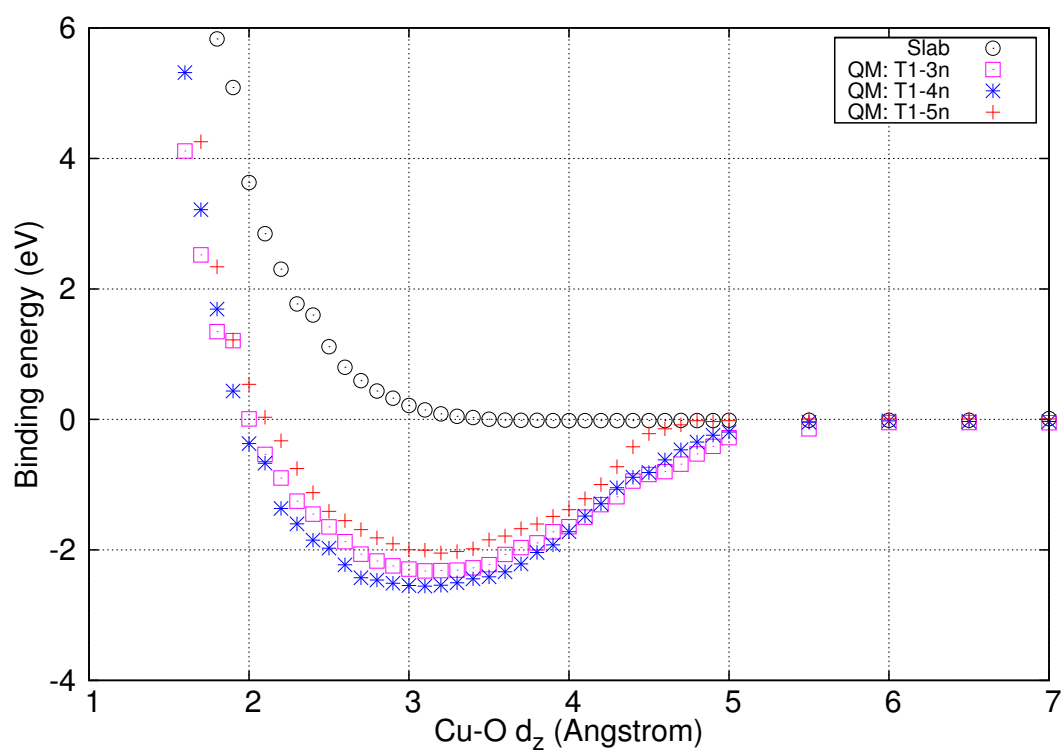


Figure 6.26: Binding energies of H₂O with a fixed orientation to the $(\bar{1}\bar{1}2)$ cluster surface against perpendicular distance of Cu-O for various QM region sizes. The corresponding binding energy for the slab system is shown for comparison.

of less than 0.1 eV. While in general the EDOS computed using the embedded cluster methodology more closely matches the DOS of the corresponding slab with increasing QM region, some but not all features of the slab DOS are reasonably reproduced. In particular, the bandwidth of 3d-Fe bands, both unoccupied and occupied, are significantly overestimated under the cluster model. The band gap of $(\bar{1}\bar{1}2)$ computed using the cluster model also underestimates that of the periodic model by 0.5 eV. In the embedded cluster study of TiO₂ surface by Berger *et al.* in which a cluster QM region of 138 atoms was employed, a strong match between cluster and periodic slab DOS was observed [188]. It is therefore possible that a larger QM region than those considered in this work is a necessity for an accurate reproduction of the periodic DOS.

All other factors, including the presence of MM or embedding charges, the MM charge scaling factor, the inclusion of an interface region consisting of cationic pseudopotentials were concluded to have limited influence in describing the correct electronic structure. The procedure used to determine the optimal scaling factor for the MM point charges was validated as near that scaling factor the Mulliken charges in the outer part of the QM region reached a minimum. However, the MM point charges were determined to have only a short-range effect on the electronic structure and hence have a negligible role influence on the inner QM region close to the active site. This is consistent with the observation made in Section 6.1.2 that the error due to the MM point charge model is only dominant within 3.5 Å of the outermost point charges.

While the electronic structure is reasonably well described by the QM/MM embedded cluster methodology, this was unequivocally not the case with regards to the potential energy surface and relaxed geometry. Geometry optimisation performed on clusters resulted in considerable distortion of the original slab geometry, and for optimisations with large active regions, inward collapse of the surface structure was observed. This is perhaps due to two shortcomings of the methodology. First, the MM region consists of merely point charges kept frozen during optimisation hence polarisation of the MM region due to changes in the geometry is not modelled. Consequently, self-consistent polarisation between the QM and MM regions, which may have stabilising influence on the system, is not described. Second, it is possible that the embedding charges, which aim to reproduce the long-range electrostatic potential, are poorly parameterised. This would result in poor representation of the potential energy, resulting in poor atomic forces. It is also important to note that the fact that no systematic improvement of the cluster relaxed geometry with increasing QM region size is observed suggests that the size of the QM region is not a main cause for the inability of the finite cluster methodology to reproduce the periodic QM potential energy surface.

Calculations of H₂O adsorption on both periodic and cluster surfaces provide further evidence of the inability of the QM/MM embedded cluster methodology to correctly describe the potential energy surface. Contrasting adsorption behaviour was observed when comparing the periodic and cluster systems. Weak binding of H₂O to the surface was predicted in the former, while strong binding was predicted in the latter. The relaxed geometry of adsorbed H₂O also differed in the two models.

In conclusion, the developed embedded QM/MM methodology in its current form is clearly not suitable for study of Cu dissolution as it provides an extremely poor description of atomic forces and optimised geometries. It is suggested that this is due to poor description of long range bulk electrostatic interactions, attributed to poorly parameterised embedding charges and the lack of self-consistent polarisation between QM and MM regions due to the fixed point charge representation of the MM region. However, given that the methodology provides a reasonable description of electronic structure, it could potentially form the basis for future development of more sophisticated and robust methods. This would likely require the parameterisation of a polarisable force field specifically for CuFeS₂ surfaces. If the force field includes short range repulsive terms, the MM region could then be allowed to relax during optimisation, further improving the description of polarisation. Moreover, the long range electrostatic interactions in the QM region can be improved by determining a more refined set of reference partial charges used to parameterise the embedding charges.

6.4 Conclusions

In this chapter, the development and evaluation of methodology for the purpose of studying Cu dissolution has been reported. The methodology is based on the QM/MM embedded finite cluster methodology developed by Sokol *et al.* for study of reactivity on ionic surfaces.

Due to the lack of an available force field for CuFeS₂ surfaces in addition to failed attempts to derive one, a simpler point charge representation of the MM region was employed. The magnitudes of the atomic centred MM point charges were specified to be the Mulliken charges scaled by a factor parameterised such that the resulting classical electrostatic potential above the surface closely matched the QM counterpart.

The accuracy of the developed methodology was assessed through systematic tests involving single point calculations and geometry optimisations on the gas phase CuFeS₂ surface, as well as simulations of H₂O adsorption. In particular, the effect of various elements of the methodology including the QM region size, presence of embedding

charges, MM point charges was investigated. The results from the tests show that the cluster methodology developed is able to reasonably reproduce the electronic structure obtained from corresponding periodic calculations in terms of Mulliken charges and the DOS. However, the optimised geometries and adsorption behaviour predicted by the methodology does not remotely resemble that of the periodic slabs. It was proposed that this was due to the neglect of self-consistent polarisation between the QM and MM regions due to the fixed point charge model for the MM region as well as the poor description of the long range electrostatic potential due to poorly parameterised embedding charges.

The severe shortcomings of the methodology imply that further study of the Cu dissolution is currently unfeasible without improvement to the methodology. This would likely involve the parameterisation of a polarisable force field for the MM region as well as a formulation of a way to parameterise of the embedding that more accurately reproduces the long range electrostatic potential.

7

Conclusions

The original aim of this thesis was to elucidate chemical mechanisms associated with the dissolution of Cu from CuFeS₂ in the context of extractive leaching. While the stated objective was not completely achieved, the fundamental knowledge of bulk and surface CuFeS₂ uncovered in the current work provides the foundation for understanding of CuFeS₂ surface chemistry. In addition, a hybrid QM/MM methodology has been devised and tested, and could potentially form the basis for refinement that would enable future studies of CuFeS₂ dissolution chemistry.

Chapter 4 presented a B3LYP density functional study of bulk CuFeS₂ in which the geometric, electronic and magnetic properties were investigated. The atomic structure and antiferromagnetic ground state of the bulk was found to be in good agreement with theory and experiment hence providing validation of the B3LYP methodology. Analysis of the electronic structure confirmed the Cu⁺Fe³⁺S²⁻ formal oxidation state and deduced the mixed ionic-covalent character of CuFeS₂ in which Fe sites are mostly ionic and Cu sites are considerably covalent in character. The slight covalent nature of Fe-S interactions was used to account for the lower than expected magnetic moment of Fe.

Chapter 5 presented a B3LYP density functional study of the surface morphology of CuFeS₂. Tasker's classifications and analysis of the coordination of surface atoms were used as tools to filter the low index surfaces down to a narrow set of potential stable surfaces which were studied at the *ab initio* level. The nonpolar (102), (110) and (114) surfaces were found to be stable with low associated surface formation energies. The optimised structure of these surfaces were found to be similar with inward relaxation of metal cations resulting in the exposure of sulphur at the surface. The defect stabilised polar (112)/($\overline{112}$) surface pair was found to be remarkably stable and thermodynam-

ically lower than nonpolar surfaces. The stability of the surface pair was attributed to a combination of geometric relaxation and charge transfer, occurring mainly at the (112) surface. However, the planar averaged potential showed that there remained a non-zero electrostatic dipole moment, which meant that the computed surface energies of the (112)/($\bar{1}\bar{1}\bar{2}$) are probably not meaningful. Nevertheless, it is suggested that the {112} surfaces are likely to be stable based on theoretical and experimental studies of isostructural I-III-VI compounds. Finally, Wulff constructions generated under a range of growth conditions predicted that the (110), (112) and ($\bar{1}\bar{1}\bar{2}$) are likely to be the predominant surfaces exposed upon fracture.

Chapter 6 described the development and evaluation of a QM/MM embedded cluster methodology devised for the purpose of future studies of Cu dissolution. A parametrised point charge representation was used to model the MM region due to the difficulty of parametrisation of a reliable force field for CuFeS₂ surfaces. A series of tests were conducted, involving calculations on the CuFeS₂ (110) and ($\bar{1}\bar{1}\bar{2}$) surfaces, to evaluate the robustness of the methodology. The methodology was found to be capable of reproducing the electronic structure of corresponding periodic systems for a fixed geometry without incurring a steep computational expense. However, the methodology was found to be completely incapable of reproducing the correct optimised geometry. This was attributed to the combination of the lack of self-consistent polarisation across the QM and MM regions, and inaccurate description of long range electrostatic interactions due to poorly parametrised embedding charges.

Further development of the methodology is required to address its current shortcomings prior to deployment in studies of CuFeS₂ dissolution chemistry. This would likely involve parameterisation of a polarisable MM force field that not only provides a reliable description of CuFeS₂ surface properties but also ensures that self-consistent polarisation between QM and MM regions is modelled. It is possible that functional forms more complicated than those considered in this work or the inclusion of three-body or higher order terms may be necessary in such a potential. In addition, the embedding charges should be parameterised from a more representative set of reference charges that faithfully reproduces the bulk electrostatic potential.

Following the development of a robust methodology that enables study of CuFeS₂ surfaces under an explicit bulk liquid environment, various aspects pertaining to Cu dissolution can then be investigated in future research. The structure of the interfacial region, termed the electrical double layer, could be probed to determine its influence on the surface diffusive properties of bulk water and electrolytes, which in turn governs the availability of potential oxidative species at the surface. The influence of water on

the surface could be studied to identify relevant active sites and hence allow speculation of the initial dissolution mechanisms. The nudged elastic band method is likely to be a useful tool to study the reaction path between an initial undissolved state and a final dissolved state. It could allow dissolution reaction barriers for various surfaces to be computed, which could in turn lead to estimation of dissolution rates. Furthermore, the species involved in charge transfer can be determined from analysis of the evolution of the electronic structure over the reaction path. Detailed study of the resulting surface properties following Cu dissolution could be used to identify possible species responsible for passivation. Information gained from studies proposed here, combined with results from relevant experimental studies, will assist in achieving the ultimate aim of deducing dissolution and passivation mechanisms and determining favourable dissolution conditions that should be adopted in practice to maximise dissolution rates and yields.

Appendix A

Basis Sets

The basis sets of atom-centred Gaussian functions used to describe the copper, iron and sulphur atoms in the current work are provided in this appendix. For each shell, the exponents of the primitive Gaussian type orbital, α_j , and the expansion coefficients for the formation of the contracted Gaussian type orbital, c_j , are listed.

A. BASIS SETS

Copper atoms are described by a 86-4111 d (41) contraction [one s , five sp , and two d shell(s)]

Shell type	α_j	c_j	
1s		s	
	398000.0	0.000227	
	56670.00	0.001929	
	12010.00	0.011140	
	3139.000	0.050130	
	947.2000	0.170310	
	327.6800	0.369600	
	128.3900	0.403000	
	53.63000	0.143700	
2sp		s	p
	1022.000	-0.004870	0.008500
	238.9000	-0.067400	0.060630
	80.00000	-0.124200	0.211800
	31.86000	0.246600	0.390700
	13.33000	0.672000	0.396400
3sp	4.442000	0.289000	0.261000
		s	p
	54.70000	0.011900	-0.028800
	23.26000	-0.146000	-0.074100
4sp	9.920000	-0.750000	0.182000
	4.013000	1.031000	1.280000
5sp		s	p
	1.582000	1.000000	1.000000
6sp		s	p
	0.596000	1.000000	1.000000
3d		s	p
	0.150000	1.000000	1.000000
		d	
	48.54000	0.031000	
	13.55000	0.162000	
4d	4.520000	0.378000	
	1.470000	0.459000	
5d		d	
	0.392000	1.000000	

Iron atoms are described by a 86-4111 $d(41)$ contraction [one s , five sp , and two d shell(s)]

Shell type	α_j	c_j	
1 s		s	
	315379.0	0.000227	
	45690.00	0.001900	
	9677.300	0.011100	
	2520.880	0.050100	
	759.7460	0.170500	
	262.9640	0.369240	
	102.8010	0.403300	
	42.97330	0.143400	
2 sp		s	p
	798.2620	-0.005200	0.008500
	191.1620	-0.068000	0.060800
	63.68850	-0.131400	0.211400
	25.36250	0.251700	0.394400
	10.73380	0.643300	0.398000
	3.764000	0.282500	0.225100
3 sp		s	p
	48.14340	0.012200	-0.021500
	17.45790	-0.227800	-0.085100
	6.997200	-0.880100	0.201000
	3.079100	0.975500	1.302400
4 sp		s	p
	1.313700	1.000000	1.000000
5 sp		s	p
	0.562500	1.000000	1.000000
6 sp		s	p
	0.225000	1.000000	1.000000
3 d		d	
	30.48210	0.058300	
	8.692000	0.259100	
	3.100800	0.516200	
	1.170900	0.565600	
4 d		d	
	0.434500	1.000000	

A. BASIS SETS

Sulphur atoms are described by a 86-311 $d(1)$ contraction [one s , four sp , and one d shell(s)]

Shell type	α_j	c_j	
1s		s	
	109211.00	0.0002520	
	16235.206	0.0019934	
	3573.0286	0.0111177	
	943.23811	0.0498945	
	99.914226	0.1661455	
	38.602137	0.3627018	
	15.531224	0.4108787	
	42.97330	0.1457875	
2sp		s	p
	281.22171	-0.0057780	0.0081427
	67.106575	-0.0665855	0.0565570
	21.794135	-0.1203552	0.2039582
	8.2097646	0.2741310	0.3973328
	3.4178289	0.6463829	0.3946313
	1.5452225	0.2925792	0.1544345
3sp		s	p
	4.3752432	-0.1750000	-0.0613439
	1.8096201	-0.5938952	0.1272251
	0.6833985	0.8298996	1.2215893
4sp		s	p
	0.2413000	1.0000000	1.0000000
5sp		s	p
	0.1060000	1.0000000	1.0000000
3d		d	
	0.3830000	1.0000000	

Appendix B

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