Hydrocarbons on Metallic Surfaces: A Quantum Mechanical Study

Elizabeth Margaret King

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This thesis has been composed by myself and it has not been submitted in any previous application for a degree. The work reported within was executed by me unless otherwise stated.

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Abstract

The binding of liquid crystal molecules to surfaces in liquid crystal cells is a difficult interaction to characterise as the environment which surrounds the liquid crystal molecules makes the system inaccessible to experimental and theoretical studies. However, insight may be gained from an examination of simplified systems which represent specific aspects of this interaction. First principles electronic structure calculations based on planewave density functional theory allow the adsorption of an isolated molecule on an extended surface to be examined and compared with studies on complex molecules.

One possible binding interaction between a liquid crystal molecule and a metallic surface may be represented by the interaction of a conjugated $\pi$ system with a metal. In order to characterise this interaction, this thesis examines the interaction of ethylene with aluminium and copper, and benzene with copper. The electronic interaction which occurs between the species can be rationalised by an identification of criteria which are important for the formation of a chemical bond in a complex molecule and an examination of whether these criteria can be met on adsorption of the hydrocarbon on an extended surface. It is found that ethylene is physisorbed on the s–p metal aluminium surface, but can be chemisorbed on the transition metal copper surface. Benzene can also be chemisorbed on a copper surface at certain sites. These results are explained by an examination of the Al(C$_2$H$_4$), Cu(C$_2$H$_4$) and Cu(C$_6$H$_6$) complexes.
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Chapter 1

Introduction

The characterisation of organic molecules on transition metals is a current topic of interest for experimental and computational studies. The aim of these investigations has been to gain a fundamental understanding of processes such as catalysis, corrosion and the growth of thin films. However, an understanding of the processes on a molecular scale remains elusive due to the complexity of the systems. Previous work has concentrated on the adsorption of small molecules such as $N_2$ [1, 2, 3, 4, 5], NO [6, 7, 8, 9] and CO [10, 11, 12, 13] on transition metal surfaces but precise characterisations of larger adsorbates are harder to obtain. Techniques such as low energy electron diffraction (LEED) [14] which determines the structure of adsorption systems, and photoelectron spectroscopy [15] which determines the electronic structure, are used to determine the salient features of the system such as adsorption site, adsorbate orientation and strength of the interactions between the species. Characterising both surface and adsorbate si-
CHAPTER 1. INTRODUCTION

multaneously is difficult to do within a single experiment, so a complete picture of the adsorption process is constructed using a combination of approaches such as LEED (low energy electron diffraction), HREELS (high resolution electron energy loss spectroscopy), TPD (temperature programmed desorption), RAIRS (resolved angle infra red spectroscopy) [16, 17] combined to examine ethylene on a copper surface.

Computer simulation provides a powerful tool for characterising the nature of adsorption, and also allows a visualisation of the system. The simulation of a complete adsorption system is not practically feasible due to the problem of representing an infinite surface and the solid below the surface though, so calculations usually concentrate on representations which capture the relevant physics of the system. Some adsorption systems can be assessed by examining a complex molecule [18], or representing the metal surface as a cluster of metal atoms [18, 19, 20]. The use of these approaches is justified by considering that characteristics, such as bond lengths within organometallic complexes, are very similar to the characteristics of an isolated molecule adsorbed on a metal surface. This can be explained by considering that the metal surface $d$ states can be hybridised with the molecular orbitals of the correct symmetry on the adsorbate to form a series of bonding and anti–bonding states similar to those found in the corresponding complex. The planewave density functional theory (DFT) calculations [21, 22, 23, 24] used here allow an extended surface to be represented by a slab of metal atoms placed in a periodically repeating supercell. This has
been successfully used to examine H₂, O₂ and CO on transition metal surfaces (for example [25, 26, 27, 28, 29, 30]).

The study presented in this thesis uses computer simulation to examine the adsorption of conjugated organic molecules on metallic surfaces with a view to providing insight into how liquid crystal molecules preferentially align and bind to a metallic substrate. As will be seen in subsequent chapters, the properties of the systems characterised in attaining this goal can also be applied to gaining a deeper understanding of heterogeneous catalysis, thin film technology and organometallic chemistry.

The alignment of nematic liquid crystal molecules with interfaces in liquid crystal cells is of interest for the improvement of the operation of the cell. Nematic liquid crystal molecules are rod like organic molecules which typically consist of a conjugated core of linked benzene rings with an alkyl tail at one end and a polar group, typically a cyano group, at the other. The way they anchor onto a metal surface gives insight into the molecular processes which occur in liquid crystal cells. To date most studies have modelled the system by approximating the liquid crystal molecule to a rigid rod with a permanent dipole moment, so leaving out the molecular detail, to ascertain how the molecules align at a surface [31, 32, 33]. The molecular electric dipole can be defined by two charges, q⁺ and q⁻, separated by a distance, l, and represented by a vector directed from q⁻ to q⁺ (although conventionally drawn in the opposite direction). The magnitude of this electric dipole is the electric dipole moment μ = ql.
Although there are many factors which influence the molecular processes, the study of the adsorption of conjugated molecules such as ethylene or benzene onto metal surfaces provides a suitable starting point for pinpointing important processes in the anchoring process.

Firstly this study characterises the geometry and electronic structure of a fluoro substituted terphenyl molecule, a molecule which is the core of many liquid crystals, in order to understand the effects of a polarising substituent on a conjugated electron system. Similar systems have previously been characterised [34, 35, 36] but there is a possibility in this molecule that the torsional angle could affect the direction of the molecular dipole moment, and so influence the alignment of molecules in the liquid crystal phase. Then the nature of the adsorption of ethylene on aluminium is determined to understand how a C-C $\pi$ bond interacts with the s–p band of a metal. There have been comparatively few studies which examine the adsorption of organic molecules on an aluminium surface [37, 38, 39], so the role of the s–p band in adsorption remains elusive. Finally the adsorption of both ethylene and benzene on copper is characterised in order to understand how a conjugated electron system binds to a transition metal surface. Both these systems have received attention [40, 41, 17, 42, 43], but their characteristics are still under debate. This study does not tell us directly about the processes involved in the binding of a liquid crystal molecule to the surface. However, from an understanding of how the conjugated electron structure of the benzene ring binds to the surface, the orientation of a liquid
crystal molecule, which contains phenyl rings in its core may be explained.

### 1.1 The Characterisation of Conjugated Molecules on Metallic Surfaces

In order to understand how processes such as the alignment of liquid crystals occur, it is essential to appreciate what is happening on the molecular scale. Adsorption systems such as these are complex. In an industrial scale adsorption system the structure of the surface is seldom perfect, often containing defects which can influence the site of adsorption. Also other adsorbates already present on the surface can influence further adsorption by affecting the geometry and electronic structure of the substrate and interacting with the new adsorbate. Much information may be gained from a detailed understanding of how an isolated molecule preferentially binds to a surface. The behaviour of the adsorbate in different environments may be understood from an estimation of how the new environment affects the preferred adsorption configuration of the isolated molecule. While the characterisation of complex systems on the molecular scale is a complex problem, insight may be gained from the examination of smaller systems selected to include the salient features of larger systems. The computer simulations performed here concentrate on the nature of adsorption of a single molecule on an extended surface.

Unsaturated hydrocarbon molecules usually bind irreversibly on transition
metal surfaces. On adsorption they may retain their gas phase geometry, rearrange or dissociate. The substrate may also be relaxed or reconstructed on adsorption. What happens is dependent on the species involved, the plane of the metal surface and its smoothness, the temperature, and the coverage by the adsorbate. From an understanding of how ethylene and benzene are adsorbed, generalisations may be extended to predict the adsorption behaviour of other unsaturated hydrocarbons. It has been reported that ethylene can be bound as ethidyne, losing a hydrogen atom [44, 45], or as C=CH₂ [46], or bound with the C–C bond parallel or tilted slightly to the surface plane [40, 47, 48] on transition metal surfaces. At low coverages benzene generally lies flat on the surface and can be distorted, the degree and nature of which is dependent on the metal and the surface plane [49, 50, 51, 52, 53]. The C–C bond lengths in the unsaturated hydrocarbons are usually elongated on adsorption and the bond order is reduced which indicates a charge transfer from the adsorbate to the metal surface. This is confirmed by an accompanying decrease in the work function of the metal on adsorption of organic molecules. Care must be taken with an extension of the generalisation to conjugated molecules containing a functional group as there is often a choice of bonding site on the adsorbate, and therefore orientation on the surface. For example in pyridine (C₅H₅N) it is possible to bind through the π ring or through the nitrogen which results in a tilting of the molecule on the surface [54]. Many such molecules tend to lie with their π rings parallel to the surface at low coverages, but lie perpendicular to the surface, bonding via the
functional group at higher coverages.

1.2 Characteristics of Conjugated Molecules, Surfaces and Adsorption systems

The use of computer simulation allows the determination of the geometry and the electronic structure of a system. From this more information, such as the nature of chemical bonding or magnitude and direction of molecular dipole moments, may be deduced. The following sections outline what may be determined about the physics of different systems using computer simulations which take only the atomic numbers of the species involved and fundamental constants as their input, so called *ab-initio* methods.

1.2.1 Conjugated Molecules

Information about the physical and chemical characteristics of a molecule may be gained from only knowing its equilibrium geometry. Just the shape of the molecule can suggest possible reaction sites and how the molecules may align in the solid phase [55]. The size of various substituents within the molecule can influence the degrees of freedom within the molecule.

There are various approaches to describing the electronic structure of molecules which are based on the electronic Schrödinger wave equation such as valence bond theory [56] and the ligand field theory[57] for complex molecules. In this
study use is made of molecular orbital theory where molecular orbitals are constructed from linear combinations of valence atomic orbitals of the correct energy and symmetry on the constituent atoms [58]. This theory is used as it can be applied to the study of complexes and chemisorption systems as well as molecules as explained below. The electron distribution associated with a particular orbital is given by the square of the wavefunction which indicates areas of charge accumulation and depletion. This link between the molecular orbitals and features in the shape of the electron density surface allows the nature and directions of the bonds between groups in a molecule to be classified and the location of possible reaction sites on the molecule to be identified.

Much of the chemistry of different molecules is rationalised by consideration of competition between steric and electronic effects. The equilibrium structure predicted from the lowest energy electron configuration may not be the same as that predicted when steric repulsions between groups in the molecule are taken into account. The true equilibrium geometry is a compromise which balances both effects. This competition between electronic and steric effects not only influences the torsional angle in a molecule as shown in chapter 3, but also can be used to assess possible surface reconstructions and favourable adsorption sites.
1.2.2 Surfaces

A surface which is formed by cleaving the solid material along a particular crystal plane, commonly relaxes or reconstructs its geometry due to the reduction in co-ordination of the atoms in the surface layer. A covalent solid, in which bonds between atoms can be discerned, undergoes a reconstruction to form new bonds in the upper most surface layers in an attempt to regain the bulk co-ordination number or a co-ordination number as close to the bulk one as possible for the surface atoms. A metallic surface with a delocalised electron structure is more likely to experience only a slight relaxation often involving a reduction in the distance between the top two planes in order to stabilise the top surface plane. The extent of relaxation or reconstruction is also dependent on which surface plane is being examined.

The appropriate theory for describing the electronic structure of crystal surfaces is the band theory as used for the solid state. The surface electronic structure is dependent both on the material and the surface plane being studied. There are surface analogues for the density of states and band structure: for the surface density of states, the states may be localised to a particular surface plane, and for the surface band structure a two dimensional Brillouin zone may be used in which the bands are determined from the $k$ vectors directed parallel to the surface. Many of these surface band structures have features which are similar to the bulk material. For example in free electron metals such as $s$-$p$ metals, the bands are broad and diffuse and do not have any local structure,
but for tight binding solids, the bands are much narrower and bonds may be discerned between atoms. The energy, width, shape, degree of localisation and occupation of the states within these bands largely determine the chemistry at the surface.

1.2.3 Adsorption Systems

In static calculations the location of the adsorption site can be determined by comparing the relative energies of the system when the adsorbate is placed at different sites with different orientations, the preferred site having the lowest energy. This is provided that there are no obstructions on the surface which could result in the selection of the preferred site on consideration of kinetic effects. This site and orientation are dependent on surface coverage and there are often different adsorption configurations at low and high coverages. Usually the adsorption configuration at low coverage is the most favourable, but as the coverage increases the structure of the surface is affected and the existing adsorbates restrict the approach of any new adsorbate so a different configuration has to be adopted. This allows an overall lowering of the energy when the coverage reaches a certain point but there is still an energy barrier to adopting a different configuration.

The appropriate approach for describing the electronic structure of adsorption systems is dependent on the strength of the interaction between substrate and adsorbate. Two types of interaction may be defined: the weaker physisorp-
tion and the stronger chemisorption interaction. Physisorption occurs due to a long range van der Waals type interaction caused by a fluctuating dipole on the adsorbate inducing a dipole on the surface which causes the two to be attracted to one another for example. No build up of electron density between the species is observed and the distance between adsorbate and substrate is typically about 3Å. A chemisorption interaction takes place when the adsorbate sticks at an appropriate site and there is a build up of electron density between adsorbate and substrate which results in chemical bond formation. The distance between the species is then less than 3Å corresponding to a typical chemical bond length. For chemisorption it is possible to describe the bonding between adsorbate and substrate in terms of molecular orbitals. Here, new molecular orbitals are created from the highest occupied molecular orbital (HOMO) and other molecular orbitals close to this in energy with localised states on the surface. The formation of these new molecular orbitals lowers the energy of the system making chemical bond formation favourable. The ability of the species to form these bonds often determines the preferred adsorption site as the adsorbate must align in order to provide an orbital of the correct energy and symmetry to bind to the surface.

The challenge of characterising adsorption systems on the molecular scale using computational calculations is that the concepts used to explain the geometries and electronic structures of the surface and molecule have been developed using different approaches. The planewave density functional theory approach
used in this study though has been used to characterise molecules [59], surfaces [29], and adsorption systems [60]. These calculations are therefore able to encompass the localised molecular orbital picture used to describe the electronic structure of molecules and the band structure of solids and surfaces. This allows the nature of the binding between surfaces and adsorbate molecules to be determined by examining the electron density distributions associated with one electron wavefunctions [61, 62].

1.3 Outline of Thesis

An overview of Density Functional Theory and how this theory is implemented in the CASTEP [21] and VASP [22, 23, 24] codes is given in chapter 2 as well as an explanation of why this particular approach is especially suited to simulations of conjugated molecules and adsorption systems.

Chapter 3 details the investigation into the dependence of the molecular dipole moment on torsional angle in fluoro substituted terphenyl molecules.

The adsorption calculations are described in the next three chapters. For all systems calculations are done to characterise a complex molecule selected to represent the adsorption system, the isolated surface and the adsorption of a single molecule on an extended surface. The nature of the adsorption of ethylene on the $s-p$ metal aluminium is determined in chapter 4. The purpose of this study is to give an understanding of how a C–C $\pi$ bond may bond to the diffuse
s–p metal band or a nearly free electron metal. This may then be contrasted with the adsorption of ethylene on copper which is detailed in chapter 5 where the binding to the surface is likely to be dominated by the narrow and directional $d$ band. The binding of a conjugated organic molecule on a transition metal surface is characterised in chapter 6 which investigates the bonding between benzene and a copper surface.
Chapter 2

Details of the Calculations

2.1 Introduction

The use of computer simulation allows systems which are unstable to be characterised and the examination of systems under conditions which cannot be reproduced in the laboratory. Computer simulations can complement existing experimental results and indicate which properties and systems would be of interest in an experimental study.

The aim of computational techniques is to determine the relative energies of systems with different atomic configurations, which allows stable geometries to be identified, and properties of systems such as molecular dipole moment, work function, etc. to be determined. There are many approaches to characterising molecules and materials which vary in their computational efficiency, transferability, reliability and accuracy. Their performance is related to their compu-
tational efficiency and accuracy, usually the greater the accuracy required, the greater the computational resources required.

Quantum mechanics is the appropriate theory for determining and interpreting the physical and chemical properties of systems on the molecular scale. The motion of electrons and nuclei in most molecules is described by the solution to the non-relativistic time independent Schrödinger wave equation from which all properties of the system which may be known are determined. Although the theory is accurate in principle, the solution of the wavefunction requires a description of the interactions between all nuclei and electrons which results in a N-body wavefunction. An analytical solution of this many body problem has proved intractable, but approximations can be made to enable the determination of various molecular properties numerically using computer simulations.

The most exact of the computational approaches for determining molecular scale properties aim to calculate the energy of a given system using only the atomic numbers of the constituents as input apart from the fundamental constants, these are so called *ab-initio* techniques. Conventionally all *ab-initio* computational chemistry approaches are based on the N-body Schrödinger equation. The Hamiltonian in the Schrödinger wave equation includes terms to take account of the kinetic energy and the Coulomb potential between all the particles in the system.

The different approximations made in computational chemistry calculations mean that it is important to understand or anticipate the nature of the system.
and the physical properties to be calculated when selecting a technique. The accuracy and reliability of different approaches are judged by comparison with more accurate calculations and experimental results. The aim of developing new techniques is to reproduce the characteristic physical properties of systems, enabling the technique to be transferable to as many different systems as possible, while being computationally efficient.

An approximation made in many calculations is the Born–Oppenheimer approximation in which the wavefunction for the system is split into wavefunctions to describe the motion of the nuclei and electrons separately. This is justified by considering the difference in mass between nuclei and electrons. As electrons are much lighter than the nuclei, the electrons are able to respond virtually instantaneously to changes in the nuclear conformation. The electrons can then be considered to be influenced only by the positions of the nuclei and are not affected by the nuclear momenta. A potential energy surface can then be created where the total energy of the system is plotted as a function of the nuclear co–ordinates, minima in the energy corresponding to stable conformations of the system and the global minimum corresponding to the ground state structure. From examining the potential energy surface, different stable conformations can be identified and the energy barrier separating the different structures may be determined. This gives the relative stabilities of the different conformations.

Using the Born–Oppenheimer approximation, the problem faced by computational chemistry calculations has become the solution of the electronic wave-
function for a set of fixed nuclear co-ordinates. This is solved numerically in most cases by obtaining a self consistent solution of the total energy determined by the electronic Schrödinger wave equation.

The wavefunction may be expanded in a basis set which usually consists of combinations of Slater and/or Gaussian functions. As a complete basis set is unfeasible, the basis set is reduced but designed to reproduce the salient features of the molecular orbitals. They are often constructed to resemble the atomic orbitals of the constituent atoms and extra functions are included to take account of polarisation functions which account for polarising groups within the molecule. The aim is to generate the minimal basis set to reduce computer time but to make it as near to complete as possible to retain the required accuracy. The self consistent field is then applied, which is based on the variational principle, to solve the one electron Schrödinger equation. A starting trial wavefunction is generated and the basis functions are varied until the minimum energy is obtained.

The accuracy of this approach is determined by the potential applied in the Hamiltonian and the basis set used. An initial approximation to the potential was made by Hartree who included just the Coulomb interactions between the electron and the ions and other electrons. This was done by determining wavefunctions from a one electron Schrödinger equation where the potential is the
CHAPTER 2. DETAILS OF THE CALCULATIONS

sum of the ion–electron coulomb interaction:

\[ V_N(r) = \sum_I \frac{Z_I e^2}{4\pi \varepsilon_0 |r - R_I|} \]  \hfill (2.1)

and the Hartree potential which includes the electron–electron interaction by calculating the coulombic interaction of each electron with the total electronic charge density:

\[ V_H(r) = e \int \frac{\rho(r')}{{4\pi \varepsilon_0 |r - r'|}} dr' \]  \hfill (2.2)

Including these potentials in the Schrödinger equation gives the following for the \( i \)th electron:

\[ -\frac{\hbar^2}{2m} \nabla^2 \psi_i(r) + (V_N + V_H)\psi_i(r) = \varepsilon_i \psi_i(r) \]  \hfill (2.3)

Although orthogonality of the eigensolutions was enforced to take account of the Pauli exclusion principle, wavefunctions which were symmetric on electron exchange which neglected the fact the electrons are fermions and the wavefunction should change sign on exchange of particles. The electron exchange and correlation potential which is a result of the interactions between electrons of identical and opposite spins was therefore not included. The exchange interaction between electrons of the same spin is a result of the Pauli principle which states that no two electrons can be in the same state and so cannot be in the same place. This effect is small but significant in determining many chemical properties which can depend on a difference in energies of only a fraction of
an eV. The exchange part for electrons of the same spin was included in the Hartree–Fock Hamiltonian by ensuring that the wavefunction is antisymmetric when electrons are exchanged.

The CASTEP (Cambridge Serial Total Energy Package) [21] and VASP (Vienna ab-initio Simulation Package) [22, 23, 24] codes used in this study implement Density Functional Theory (DFT) which is based on determining the ground state energy from the ground state electron density instead of from the Schrödinger wavefunctions. This theory, which was originally developed for studying solid state systems, is described in detail in the following section. The stable nuclear geometries are then determined by reducing the Hellmann–Feynman forces which act on each nucleus.

This chapter gives a brief overview of DFT and how this is implemented in the computer codes. This is followed by an explanation of how this technique is applied to studying adsorption systems and how the electronic structure of such systems can be interpreted.

### 2.2 Density Functional Theory

Density Functional Theory (DFT) is the proof by Hohenberg and Kohn [63] that the total energy of a system is a unique functional of the electron density of the system. The minimum energy corresponds to the ground state energy and electron density of the system, and it is only the ground state values which
have physical significance. In Density Functional Theory it is the electron density which is the variable quantity used to determine the energy. This theory is exact in principle but the form of the functional is not known. However, approximations can be constructed by considering all possible interactions involving electrons in a given system.

Initially Hohenherg and Kohn attempted to solve this functional by dividing it into parts to describe the kinetic energy of the electrons, the attraction between the electrons and atomic nuclei, and the electron-electron interaction which can be divided into a Coulombic repulsive part and a correlation interaction which included the effects of electron exchange. These are the same interactions that were considered in formulating the Hamiltonian used in the Hartree–Fock approach for the determination of the electronic structure. To make this practically applicable to material systems, Kohn and Sham [64] split the electron kinetic energy into a part which could be solved exactly for a non-interacting electron gas and included the remainder in the electron exchange and correlation term which is included explicitly in the functional:

$$E[\rho] = -\frac{\hbar^2}{2m_e} \sum_{i=1}^{n} \int \psi_i^*(\mathbf{r}_i) \nabla_i^2 \psi_i(\mathbf{r}_i) d\mathbf{r}_i$$

$$- \sum_{i=1}^{N} \int \frac{Z_i e^2}{4\pi \varepsilon_0 r_{1i}} \rho(\mathbf{r}_i) d\mathbf{r}_i$$

$$+ \frac{1}{2} \int \rho(\mathbf{r}_1) \rho(\mathbf{r}_2) e^2 \frac{d\mathbf{r}_1 d\mathbf{r}_2}{4\pi \varepsilon_0 r_{12}} + E_{XC}[\rho]$$

(2.4)
Here the electron density, ρ, is defined by:

$$\rho(r) = \sum_{i} |\psi_{i}(r)|^2$$  \hspace{1cm} (2.5)

The first term in equation 2.4 is for the kinetic energy of a non-interacting electron gas of the same density as the electron density at the point being considered (where $h$ is Planck’s constant and $m_e$ is the mass of an electron). The second term is the Coulombic interaction between nuclei and electrons (where $Z$ is the charge of a specified nucleus and $e$ is the charge of an electron, $r$ is the distance between the nucleus and the electron and $\rho$ is the electron density), the third term is the Coulombic interaction between electrons (where $r_{12}$ is the distance between electrons 1 and 2), and the fourth term includes the exchange and correlation interaction as well as the correction to the kinetic energy for interacting electrons. The exchange and correlation energy may be defined from 2.4 by subtracting all the known parts of the functional from $E[\rho]$ to give $E_{XC}[\rho]$.

In order to generate a solution to this functional the Kohn–Sham equations are used which construct an effective one electron operator to give pseudo eigenvalue equations.

$$\left\{ -\frac{\hbar^2}{2m_e} \nabla^2 + \sum_{l=1}^{N} \frac{Z_i e^2}{4\pi\varepsilon_0 r_{l1}} + \int \frac{\rho(r_2)e^2}{4\pi\varepsilon_0 r_{12}} dr_2 + V_{XC}(r_1) \right\} \psi_i(r_1) = \varepsilon_i \psi_i(r_1)$$  \hspace{1cm} (2.6)
CHAPTER 2. DETAILS OF THE CALCULATIONS

The problematic many-body wavefunction is therefore transformed into the problem of solving equations for individual electrons moving in an effective potential generated by the nuclei and other electrons in a similar manner to the Hartree-Fock approach. The functional form of the part describing the exchange and correlation interaction is unknown for a varying electron density in 2.6. The exchange–correlation part can be defined in 2.6 as:

\[ V_{XC}[\rho] = \frac{E_{XC}[\rho]}{\delta \rho} \]  \hspace{1cm} (2.7)

Usually the exchange–correlation energy is obtained by considering the electron density at a point to be equivalent to that of a homogeneous electron gas of the same density. A set of values at different densities is then generated and used in the codes. One of the important effects of the exchange–correlation interaction is the formation of an exchange–correlation hole. As electrons of the same spin cannot occupy the same state according to the Pauli exclusion principle, they must be separated in space. This requires the formation of an exchange–correlation hole where there is a region of depletion in the electron density surrounding any given electron. The success of approximations to the exchange–correlation interaction largely depend on their ability to reproduce the behaviour expected from the inclusion of the exchange–correlation hole.

The local density approximation (LDA) [64] has been used for solid state calculations and is based on the solutions of \( E_{XC} \) for a uniform electron gas.
Essentially the system under investigation is divided into small volume elements and the exchange–correlation energy calculated for each element. The effectiveness of the LDA is perhaps surprising as the electron density varies rapidly as a function of position, but has been successfully applied as the effect of the exchange–correlation hole is accurately reproduced. For molecular systems the most appropriate approximation is the general gradient approximation (GGA)[25, 65]. This includes both the density and density gradient within the volume element in determining $E_{XC}$. Information is therefore included about how the electron density is changing at the point in question. This is important in systems such as molecules, where there are comparatively extreme changes in the charge density over distances of the order of atomic radii. This is also the appropriate approximation for adsorption systems as it provides a better description of the change in electron density around the adsorbed molecule. The GGA approximation is still restrictive in its inclusion of influences from changes in the charge density occurring away from the point in question. This causes problems in accounting for remote effects in the substrate in adsorption systems.

The computationally inexpensive inclusion of the exchange–correlation interaction is where DFT has been successful over other computational chemistry approaches and the formulation of accurate and efficient exchange–correlation functionals is the main way in which DFT can be improved.
2.3 CASTEP and VASP

The application of Density Functional Theory to determining molecular and material properties using computer simulations involves determining the set of electronic wavefunctions which minimise the Kohn–Sham energy functional (2.4). This is done by solving the Kohn–Sham equations (2.6) using the most appropriate approximation to the $V_{XC}$ term.

2.3.1 Implementation of a Planewave Basis Set

The CASTEP and VASP codes were originally developed for determining the physical properties of crystalline solids. The translational symmetry of such systems can be exploited to construct a framework for solving the Kohn–Sham eigenfunctions. The crystal structure is constructed from a periodically repeating unit cell, and so instead of calculating the K–S wavefunction for each electron in an infinite solid, the problem is reduced to considering only the wavefunctions of electrons within the unit cell. The representation of the crystal structure in terms of unit cells allows the application of Bloch's theorem which in turn allows the implementation of planewave basis sets to determine the electron distribution. The wavefunction for electrons in crystals, moving under the influence of a periodic potential, is the Bloch function. This is constructed by firstly considering that the potential does not change when translated an integral number of lattice spacings.

$$V(r + nR) = V(r) \quad (2.8)$$
Here $n$ is an integer and $\mathbf{R}$ the lattice spacing.

There is only a phase difference between the wavefunction at $r$ and that at $r + R$ so that:

$$\psi(r + R) = \exp(ik \cdot R)\psi(r)$$

(2.9)

It is Bloch’s theorem which allows the phase difference between $\psi(r)$ and $\psi(r + R_L)$ to be written as $(k \cdot R_L)$. This introduces the wave vector, $k$, which in this formulation labels the electronic states.

A general form for the wavefunction of electrons moving through a periodic lattice may then be written as:

$$\psi(r) = \exp(ik \cdot r)u(r)$$

(2.10)

Here $u(r)$ is a periodic function which has the same periodicity of the cell.

This convolution of a planewave and periodic function is known as a Bloch function. There is a periodic ($u(r)$) function for each band in the unit cell which is determined for each $k$ value. This band can be labelled as $j$ and then both $k$ and $j$ are required to label the electronic state. The periodic function $u(r)$ may then be expanded as a set of planewaves. Planewaves are convenient to use because of their generality and ease with which they can be made to reflect the periodicity of the reciprocal lattice by making their wave vectors reciprocal.
lattice vectors. The wavefunctions can then be written as:

$$\psi_{j,k}(r) = \exp(\imath kr) \sum_{G} c_{j,k}(G) \exp(\imath Gr)$$ \hspace{1cm} (2.11)$$

$$\psi_{j,k}(r) = \sum_{G} c_{j,k}(G) \exp(k + G)r$$ \hspace{1cm} (2.12)$$

Here $G$ is the reciprocal lattice vector and the electronic wavefunctions can now be expanded in a planewave basis set with the wave vectors taking the value of $k + G$.

The simplification of the problem by exploiting the translation symmetry of the crystal system can be applied in the Kohn–Sham equations so:

$$\sum_{G} \left[ \frac{\hbar^2}{2m} |k + G|^2 \delta_{GG'} + \tilde{V}_{eff}(k + G, k + G') \right] c_{j,k}(G') = \varepsilon_i c_{j,k}(G)$$ \hspace{1cm} (2.13)$$

Here:

$$\tilde{V}_{eff}(k + G, k + G') = \tilde{V}_N(k + G, k + G') + \tilde{V}_H(G - G') + \tilde{V}_{XC}(G - G')$$ \hspace{1cm} (2.14)$$

The periodicity is included by expanding the functions using a planewave basis set whose wavevectors correspond to the periodic lattice vectors. The coefficients of the planewaves in the expansion, $c_{j,k}(G)$, are the variational pa-
rameters used in the code as shown in fig.2.1. The size of the basis set should in principle be infinite but for practical purposes it can be made finite as the energy converges with respect to basis set size. The size of the basis set is dependent on the curvature of the wavefunction, a greater curvature requiring a larger number of planewaves. In CASTEP and VASP the number of planewaves is determined by a plane wave kinetic energy cutoff at which point the total energy of the system has converged. The wavefunctions are labelled with reciprocal lattice vectors but it is the electron density in real space which is to be determined. This is obtained by performing a Fourier transform.

2.3.2 k-point Sampling

As k can be of any value in an infinite crystal, the problem is now that a finite number of wavefunctions corresponding to the bands, should be evaluated for an infinite number of wavevectors k (k-points). However, the electron wavefunctions are very similar at neighbouring k-points and therefore need only to be evaluated at a finite number of k-points. This set of k-points must reflect the shape of the reciprocal unit cell or Brillouin zone. The total energy converges on increasing the number of k-points, so any error may be reduced by increasing the k-point density (fig.2.2). The appropriate density of k-points is dependent on how much the bands vary in energy throughout the cell in the material under investigation.

The number of k-points at which the wavefunctions need to be evaluated can
Generate the coefficients in the expansion of the wavefunction of the system.

Determine the total energy.

Update the coefficients.

Recalculate the total energy.

Ground state energy and electronic structure.

Energy at minimum.

Use minimisation technique to determine changes to coefficients.

Figure 2.1: Flow diagram outlining the method of determining the ground state electronic energy in CASTEP and VASP.
Figure 2.2: The convergence of the total electronic energy with respect to k-point density for a Cu(100) surface slab. The k-point density is increased within the surface plane.
be further reduced by considering the symmetry of the system. The inclusion of symmetry not only reduces the number of calculations required, but also ensures that the results are physical as often the symmetry of the system must be preserved during the calculation. As the energy levels at two k-points which are symmetrically equivalent must be the same, only the k-points within the irreducible Brillouin zone need be considered. The required set of k-points can then be generated by applying the point group operations associated with the symmetry of the system. This can be applied only if the wavefunctions generated using this reduced k-point set are identical to the wavefunctions generated when the k-point set spans the entire cell. Here the k-point grid is generated according to the scheme of Monkhorst and Pack [66] which creates the minimal k-point grid.

2.3.3 Supercells

Although this approach was developed for solids with a periodic structure, aperiodic systems such as surfaces and molecules may be studied with enforced periodic boundary conditions provided that the supercell is sufficiently large in order to separate the molecules from the influence of their molecules in neighbouring cells. The molecular wavefunctions need only be calculated at one k-point, conventionally taken as the Γ point in the Brillouin zone, as they do not vary in energy throughout the Brillouin zone. An interesting feature of applying these codes to the study of molecules is that the wavefunctions are expanded
as a planewave basis set in contrast to the more conventional basis sets based on hydrogenic atomic orbitals. Fortunately it has been shown that CASTEP and VASP accurately reproduce the geometries and predict chemical bonding of systems characterised using conventional computational chemistry packages [67].

### 2.3.4 Pseudopotentials

In order to make the calculations more efficient the size of the basis set may be reduced by introducing pseudopotentials to describe the electron–ion interaction. Most physical and chemical properties of materials depend only on the behaviour of the valence electrons. Therefore the potential of the nucleus and core electrons can be replaced by a weaker and smoother pseudopotential which gives a wavefunction with no radial nodes in the core region. This reduces the number of planewaves required to describe the valence electron wavefunctions which oscillate rapidly in the core region in order to maintain orthogonality with the core electron wavefunctions. The pseudopotentials are constructed so that the pseudo valence electrons experience the same potential outside the core region as the actual valence electrons.

In order for a pseudopotential to be valid it is essential that the actual wavefunction and the pseudowavefunction are identical beyond a certain cutoff radius of the atom, $r_c$, which defines the boundary of the core region. To accurately reproduce the scattering of the valence electron wavefunctions from the ion cores,
the pseudopotential should depend on the angular momentum component of the wavefunction. The simplest type of pseudopotential is the local pseudopotential which is the same for each angular momentum component. Non-local pseudopotentials have different forms for each angular momentum component and include forms for excited states to ensure transferability of the potential when the atom is placed in different electronic environments.

The criteria for generating the norm-conserving pseudopotentials used in this study are that the core charge and pseudo-electron eigenvalues are the same if produced using pseudopotentials as if produced using the complete atomic potential, and that the pseudo electron wavefunctions, and their first and second derivatives, must be continuous at $r_c$. The basis for determining a pseudopotential which complies with the above criteria is to firstly complete a full potential calculation to give the wavefunction for an isolated atom. This wavefunction is then smoothed within $r_c$ but not altered beyond $r_c$. The calculation is then inverted to determine the pseudopotential which generates this pseudo wavefunction.

The general form of non-local pseudopotentials is:

$$\hat{V}_{NL} = \sum_{lm} | Y_{lm} > V_l < Y_{lm} |$$

(2.15)

Here $Y_{ml}$ are the spherical harmonics and $V_l$ is the component of the non-local pseudopotential associated with a particular spherical harmonic.
The Kleinman–Bylander pseudopotentials used in the CASTEP code take the form:

\[ V_{KB} = V_{loc} + \sum_{lm} \left| \frac{\psi_{lm} \delta V_i}{\psi_{lm} | \delta \psi_{im}} \right| < \psi_{im} | \delta \psi_i > \]

(2.16)

A local pseudopotential which is the same for all angular momentum components is selected based on its accuracy and convenience. A term is then added which takes into account the difference between this local pseudopotential and each component of the non–local pseudopotential as:

\[ \delta V_i = V_{(non-local)} - V_{local} \]

(2.17)

The calculations done with the VASP code use Vanderbilt ultrasoft pseudopotentials [68, 69]. These allow a lower planewave cutoff energy (ie. a smaller basis set) by relaxing the norm–conservation condition. The pseudo wavefunction within the core region is no longer required to be normalised so that a smoother pseudopotential can be obtained. However, the electron density given by \( \sum_i | \psi_{i(r)} |^2 \) must be augmented in the core region in order to match the actual charge density.

### 2.3.5 Minimisation of the K–S Equations

After the first calculation has been done on the trial starting configuration, it is necessary to minimise the energy with respect to the planewave coefficients in
order to determine a self consistent solution to the energy as shown in fig. 2.1. In
CASTEP and VASP there are two procedures which can be applied to minimise
the multi-dimensional function: the steepest descents method and the conju-
gate gradients method. In the steepest descents method the search is carried out
along the direction opposite to the gradient vector until a minimum is found. A
new search direction is determined at this point, again in the direction opposite
to the gradient vector and this procedure is repeated until the searches converge
onto a minimum. The disadvantage of this technique is that no precise minimum
is determined and the ease of convergence is dependent on the function for which
the minimum is sought. In the conjugate gradients minimisation technique [70]
search directions do not need to be perpendicular to one another. Instead after
the first minimisation step which is the same as that used in the steepest de-
scents method, the new search direction is constructed using the previous search
directions. This is given by \( d_i = -g_i + \beta_i d_{i-1} \) where \( d_i \) is the search direction,
\( d_{i-1} \) is the previous search direction and \(-g\) is the negative gradient vector at
the point at which the new search will begin. \( \beta \) is a parameter which can be
determined in a number of ways, in the codes used here the form of Fletcher
and Reeves [70] where \( \beta_i = \frac{g_i g_i}{g_{i-1}^t g_{i-1}} \). In order to speed up the minimisation it
is possible to precondition [71] the first steepest descent step in the conjugate
gradient method. This is done by considering that the minimisation is a way of
reducing the error in the wavefunction, and so by aligning the initial steepest
descents vector as closely as possible with the error vector, the initial step will
lead to a more rapid convergence.

### 2.3.6 Determination of the Total Energy

To make comparisons between energies of different structures, it is necessary to include the contribution to the total energy from the interactions between ions. This Coulomb interaction is long ranged and the summation of contributions from the interactions between an ion and a lattice of ions does not converge. However, if the summation is separated into parts done over real space and reciprocal space according to the scheme of Ewald, then both summations converge in their respective spaces.

### 2.3.7 Determination of the Ground State Geometry

Once the ground state electronic structure has been determined, the equilibrium geometry of the system is obtained by moving the nuclei so that there are no forces acting on the ions. To minimise the amount of calculation time, a plausible starting configuration is generated in the supercell based on experimental interatomic distances. After the first minimisation of the electronic energy has been carried out, the forces acting on the ions can be calculated according to:

\[
\mathbf{F}_i = -\frac{\partial E}{\partial \mathbf{R}_i}
\]  

(2.18)
Here the force acting on any ion at \( \mathbf{I} \) is the partial derivative of the total energy with respect to the position \( \mathbf{I} \).

This is known as the Hellmann–Feynman force \([72, 73]\) and in order for the above to be valid the calculation must be at an eigenstate of the electron system. The ions may then be moved so that the net force acting on each atom is within a specified tolerance which would ideally be zero. It is possible to restrict the movements of the ions in order to preserve the symmetry of the system. The space group of the system is determined by the program and maintained by averaging over pairs of forces which should be equal. The total energy is minimised with respect to the atomic positions by using the steepest descents or conjugate gradients minimisation techniques as for the electronic energy.

### 2.3.8 Metals

In order to determine the Fermi level in a metal, the sampling at a large number of \( k \)-points is required. However, a lower \( k \)-point density may be used if the smearing method is employed. This entails the specification of a larger number of electronic bands than necessary, then filling them up to the Fermi level. The boundary for the filling is not determined by a step function, but by a Gaussian function, the width of which is dependent on the metal and may be defined in the calculation. This allows partial occupancy of the bands and an accurate reproduction of the Fermi surface without using a large number of \( k \)-points.
2.3.9 DFT Codes

There are parallel versions of both CASTEP and VASP in which calculations at the k-points are distributed over the processors. Due to the size of many systems of interest, the parallelisation of the planewave DFT codes allows a computationally efficient way to characterise large scale systems such as adsorption processes.

2.4 Choice of Representation of Adsorption Systems

When applying the CASTEP and VASP codes to the study of adsorption, a choice has to be made on how to represent the system within the periodically repeating supercell. This choice is dependent on the strength and extent of interactions with neighbouring adsorbates and on how localised the adsorption interaction is considered to be. The extent of localisation is dependent on the species involved, and mainly on the extent of delocalisation of the electronic structure of the substrate. The more localised the electronic structure of the substrate, usually the more localised the interaction and the less the detail required of the electronic structure of the extended surface. In this study the influence of neighbouring adsorbates is not considered as this study is only concerned with the adsorption of isolated molecules as explained in the introduction.
In situations where a strong chemical bond is formed between the species, the interaction is highly localised and it is often appropriate to explain the adsorption in terms of molecular orbitals formed between the adsorbate and a limited number of substrate atoms. This situation can be represented by a single complex molecule in which all the salient features of the interaction may be identified. If the surface reconstructs when forming this strong bond then a greater part of the surface needs to be included as a greater number of surface atoms are involved.

When physisorption or weak chemisorption occurs, long range van der Waals interactions caused by the electrostatic interactions between species are important and so a representation including an extended surface is required. An extended surface can be created in the supercell by generating a slab which is infinite in the surface plane, but finite in the direction perpendicular to this plane, the slabs being separated by a vacuum gap (fig. 2.3). The slab should be thick enough so that the surface layers have the same structure and electronic structure as if the surface terminated an infinite solid. In order to determine the relaxation of the isolated surface or reconstruction in the case of some surfaces, the positions of the uppermost layers can be relaxed keeping the lower layers fixed to represent the bulk, or both surfaces can be relaxed ensuring that the slab is thick enough so that the interlayer spacing in the centre of the slab is equivalent to the bulk lattice parameter (fig. 2.3). The thickness of the slab and the number of relaxed layers are dependent on the extent of relaxation of the
Figure 2.3: Part A shows the contents of supercells where only the top layers may relax. Part B shows the contents when both surfaces are allowed to relax but the slab must be thick enough to ensure that the spacing between the centre layers is equal to the bulk lattice parameter.

structure and the extent of surface reconstruction when an adsorbate is placed on the surface. The greater the reconstruction the greater the number of layers required to ensure that there are enough unreconstructed layers to represent the bulk material. An adsorbate can be placed at different sites on the surface slab and isolated from neighbouring adsorbates by ensuring that the cell is sufficiently large in the direction of the surface plane.

It is possible to compare the results of these complex molecule and slab approaches directly within CASTEP and VASP as the same input parameters such as type of pseudopotential and basis set size can be used for both calculations of the molecule and adsorption systems. A combination of the molecule and slab representations can be used to characterise the type of adsorption and the
nature of the bonding between adsorbate and substrate. By understanding how
the bonding molecular orbitals are constructed in the molecular calculations,
a preferred adsorption site and the orientation of the molecule on the surface
can be predicted by considering how the molecular orbitals may form bonding
combinations with the electronic structure of the metal surface. The inability
of species to form chemical bonds can also be explained if it is not possible to
generate new molecular orbitals from the combining orbitals.

2.4.1 The Characterisation of Adsorption Systems

As has been explained, the ground state structure of a system can be determined
using DFT as implemented in the CASTEP and VASP codes. The ground state
geometry, energy and electron density of the system are given in the output. The
use of CASTEP and VASP allows the influence of steric and electronic features
of the system on determining the nature of adsorption to be assessed.

The planewave DFT approach is ideally suited to determining the charac-
teristics of adsorption systems as it can be used to calculate the structures of
both molecules and surfaces. Concepts such as molecular orbitals, (taken from
the Kohn–Sham orbitals and explained in the next section) appropriate for de-
scribing the electronic structure of molecules, and the band structure of solids
can both be determined from the electron density CASTEP and VASP. This
is particularly appropriate for chemisorption where in some cases the binding
between adsorbate and substrate is best described using molecular orbitals, and
in others where a weaker binding interaction occurs, more detail about the long range distortion in the electronic structure of the surface is required. The approaches to describing the electronic structure are described in more detail in the next section.

The comparison of total energies of different configurations and examination of the relaxed geometry of adsorption systems yields much detail about the orientation of the adsorbate and nature of adsorption. By examining the equilibrium geometry for different adsorption sites, possible steric restrictions on the adsorption configuration and the influence of the surface geometry on adsorbate orientation can clearly be seen. Information about the system can be gained from studying the possible surface reconstructions and any changes in the geometry of the adsorbate on adsorption. From examining bond lengths within and the distances between adsorbates and substrates, an estimate of the strength of adsorption can be made. For example, if the surface reconstructs during adsorption, it is likely that a strong chemical bond is formed between the species as the surface has to overcome a significant energy barrier in breaking bonds between the surface atoms in order to provide a favourable arrangement for adsorption.

Adsorption energies can be determined using CASTEP and VASP by comparing the total energies of the isolated adsorbate and isolated substrate with the total energy of the adsorption system. In order to ensure that this comparison can be made it is essential that the same supercell dimensions are used
for the slab and adsorption systems with identical kinetic energy cutoffs. This is quantitatively accurate for chemisorption systems but is not as accurate for physisorption though still may be used for qualitative comparisons. This lack of accuracy is due to the problem of using the general gradient approximation in characterising a long range interaction. As the GGA only accounts for local changes in the electron density, the long range dispersion force cannot be accurately determined. By comparing adsorption energies at different sites, it is possible to estimate barriers to diffusion across the surface and therefore the mobility of the adsorbate on the surface.

An examination of the ground state electron density determines the extent of build up of charge density between adsorbate and substrate. This gives a rough estimate on the possibility of formation and the location of a chemical bond between the species. A more detailed picture can be gained by investigating the charge density surfaces corresponding to the bonding Kohn–Sham orbitals. This gives a clearer picture of which orbitals are involved in the bond and therefore why an adsorbate is chemisorbed or not at a particular site.

2.4.2 Interpretation of Electronic Structure

The geometry and reactivity of the molecule can be understood by considering features of its electronic structure. The most direct way of examining the electronic structure is to look at the electron density surface. By examining the distribution of the electron density, points where build ups or depletions in the
CHAPTER 2. DETAILS OF THE CALCULATIONS

electron density occur may be identified. The chemical behaviour of the species may be predicted by identifying reaction sites on the adsorbate molecule and on the substrate. The chemical bonds between atoms may be located by searching for a build up in the charge density along the line joining the nuclei. This can be used to indicate whether a chemical bond is formed between an adsorbate and substrate, but tells us little about the nature of this bond and why it can be formed. Another way to interpret the molecular electronic structure is is the theory of Atoms in Molecules developed by Bader [74] which identifies features of the gradient of the charge density and associates them with features of molecular structure. For instance certain critical points on the gradient surface can be associated with the positions of nuclei and chemical bonds.

A widely used concept in interpreting the electronic structure of molecules is that of molecular orbitals. These are the one electron wavefunction solutions of the Schrödinger wave equation. They are related to the distribution of the electron throughout the molecule by \( \rho(r) = |\psi(r)|^2 \). The molecular orbitals are a useful way of predicting the formation of chemical bonds between species, which can occur when combining orbitals fulfil certain criteria. These are that the orbitals are close in energy and have sufficient overlap, where the amount of overlap is dependent on the symmetry and distance between combining orbitals. The overlap integral is given by \( S = \langle \chi_A | \chi_B \rangle \) where \( \chi_A \) and \( \chi_B \) are atomic orbitals centred on different atom. The magnitude of the overlap of the orbitals determines the strength of the bond with a greater overlap integral corresponding
to a stronger bond. The closer the orbitals in energy and distance and the greater the overlap, the stronger the bond. Two appropriate orbitals combine to form two new orbitals, one of lower energy (a bonding combination), and one of higher energy (an anti–bonding combination), than the original orbitals. Occupancy of the bonding orbital results in a stabilising interaction, but if the higher energy anti–bonding orbital is also occupied, the interaction is weakened, if indeed bonding occurs at all.

Molecular orbitals can be constructed in Hartree–Fock based calculations from linear combinations of atomic orbitals. The energies of these molecular orbitals have been related to ionization energies by Koopmans' theorem. This states that the energy difference between a system and the same system with an electron removed from the $k$th orbital is shown to be equal to the ionization energy associated with an electron from the $k$th orbital [75]. A note of caution should be added that an accurate description of chemical bonding interactions using this approach is only possible if the electron correlation interaction is of little significance.

The use of the K–S orbitals from DFT has been shown to provide and effective alternative from characterising the electronic structure. Work by Stowasser and Hoffmann [76] has compared the shapes of the K–S orbitals, their symmetries, orders and eigenenergies with those produced in Hartree–Fock based calculations and found them to be similar for $\text{H}_2\text{O}$, $\text{N}_2$, $[\text{CrH}_6]^{6–}$ and $[\text{PdCl}_4]^{2–}$. Kar et al [77] have also compared the atomic charge, bond index and valence
of a number of small closed shell molecules determined with K–S orbitals with molecular orbitals from Hartree–Fock calculations and found the results not to differ significantly. The quantitative foundation for this comparison is provided by Baerends et al [78] who link the energy of the highest occupied molecular orbital (HOMO) of the K–S orbitals and the first ionization energy in a similar manner to Koopmans for Hartree–Fock orbitals. The defining features of the valence K–S molecular orbitals, such as their nodal structure and eigenenergies, are found to provide a useful qualitative approach for examining and interpreting molecular structures in a similar manner to the molecular orbitals obtained from Hartree–Fock theory.

A Mulliken population analysis [79, 80, 81] determines the electron population of different orbitals by considering which basis functions are associated with each atom. This is a commonly used analysis for interpreting the results from localised basis set approaches as the charges on and orbital populations
of the constituent parts within the molecule can be determined. The extent of charge transfer between species can then be evaluated by comparing the charges on different atoms. With planewave DFT methods, the states generated from planewave basis sets are projected onto localised basis sets and the population analysis is carried out on these projected states. The link between the delocalised planewave and localised pictures is provided by projecting the eigenstates from planewave calculations onto Bloch functions formed using localised basis sets, which are usually atomic orbitals generated using psuedopotentials from the Kohn–Sham equations. If the function is over two atoms then the associated electron density is evenly split between them. The charges on different species within the system can then be determined and charge transfer between species can be assessed. The extent of charge transfer gives information about the strength of bonding, the greater the charge transfer in general the stronger the bond.

The electron density surface can be used to give a general impression of the electronic structure of metallic solids. Contours of electron density can be used to assess whether localised bonding between atoms in a solid is occurring, and if so where these bonds lie. A plot of the electron density of the surface reveals how corrugated the density is and therefore how reactive the surface is and where adsorption sites are likely to occur. Comparisons can be made between different surfaces which can give insight into the strength of binding between surface atoms and possible adsorption sites. The CASTEP and VASP codes
allow density of states (DOS) plots to be made using the eigenstates from the Kohn–Sham equations. This gives an indication of the energies of the different bands and can be compared with bulk DOS plots to identify presence of surface states.

A distinction can be made between chemi and physisorption from the charge density surface by examining whether there is a build up of charge density between adsorbate and substrate. If there is no build up of density then it is likely that physisorption is occurring, but if there is electron density between the species then chemisorption must occur to some degree. A DOS plot can be used to determine whether the molecule remains intact on adsorption as the molecular orbitals correspond to sharp single energy peaks (fig.2.5). If these can be discerned then the molecule has not been distorted on adsorption and must only be weakly chemisorbed or more likely physisorbed. If there are fewer peaks than the number of molecular orbitals, then the peaks correspond to the orbitals which are non-bonding with the surface and the missing peaks indicate which orbitals are involved in the interaction with the surface. The charge density corresponding to different Kohn–Sham orbitals or bands of the adsorption system can be plotted to identify the molecular orbitals on the adsorbate which combine to the surface in a chemisorption interaction. This may then be compared to the K–S orbitals generated in the corresponding complex molecule calculations to identify which bonding combinations are occurring and what influence these have on adsorption site and adsorbate orientation.
Figure 2.5: A schematic density of states plot which shows a physisorption or weak chemisorption interaction between a molecular adsorbate and a metallic surface.
2.4.3 Summary

This chapter has shown how DFT applied using CASTEP and VASP can be used to characterise adsorption energies, geometries and bonding. The following chapters show how this approach has been used to characterise the bonding within a conjugated organic molecule and to characterise the adsorption of small conjugated organic molecules on two contrasting metallic surfaces, one in which the electronic structure of the substrate is delocalised (Al), and one in which it is more localised (Cu).
Chapter 3

Fluoro Terphenyls

3.1 Introduction

The determination of torsional potentials and molecular dipole moments of fluoro substituted terphenyls provides a suitable starting point for understanding the characteristic behaviour of liquid crystal molecules. The fluoro substituted terphenyls are relevant as they form the core of many liquid crystal molecules (fig.3.1), and influence some of the physical properties of these larger molecules. The interesting phase behaviour displayed by liquid crystals, where there is orientational order but the spatial coordinates are not necessarily fixed, is strongly influenced by the alignment of and interactions between the molecules. For example in the smectic liquid crystal phase shown in fig.3.2. The elongated calamatic liquid crystal molecules have orientational order, in that they are all aligned in the same direction, and are restricted spatially in planes, but these are
CHAPTER 3. FLUORO TERPHENYLS

Figure 3.1: Schematic diagram of a calamatic liquid crystal molecule. R is a chain group which can be alkyl, alkoxy, alkenyl or alkenoxy. Z is a linking group which can be a saturated group, in which case a conjugated electron structure of the core is not permissible and so the phenyl rings effectively act as independent units, or unsaturated group which allows the formation of a delocalised electron system. X is the terminal group which is usually polar, such as a cyano group. The core can be formed from a fluoro substituted terphenyl when the linking group is a phenyl and hydrogens are substituted for fluorines on the phenyl rings in the core.

the only constraints on their movement. The phase behaviour is therefore dependent on details of the structure of individual molecules such as their molecular shape, flexibility, polarisability and the presence of permanent molecular dipole moments. These molecular properties determine the alignment of the molecules and their response to external electromagnetic fields. The elongated shape of calamatic liquid crystal molecules (fig.3.1), and location of polar groups result in anisotropic molecular properties which allow the formation of a liquid crystal phase. In particular the core of the liquid crystal molecule is responsible for ensuring the rigidity of the molecule and therefore the fixed anisotropy of its shape and consequentially its molecular properties and condensed phase behaviour. This rigidity results from the electronic structure created when groups containing delocalised electron systems are joined together.
Figure 3.2: Schematic diagram showing the orientational order of calamatic liquid crystal molecules in the smectic A phase. The molecules also possess some spatial order as they are arranged in layers but are allowed more freedom to move than in a crystalline solid.

Most liquid crystal molecules are organic and have a conjugated electron system at their core. Conjugation allows the total energy of the molecule to be lowered by extending a delocalised \( \pi \) system over a part of, or the entire molecule. This often arises where there are alternate single and double C–C bonds which result in a shortening of the formal double bonds and a lengthening of the single bonds: conjugation eliminates the distinction between the bonds. This occurs in the biphenyl or terphenyl based cores where the delocalised \( \pi \) electrons around the phenyl rings can be delocalised over the whole core. The extent of delocalisation is dependent on the alignment of the phenyl rings, full
delocalisation occurs when the rings lie in the same plane and no delocalisation occurs over the molecule when the planes of the rings are perpendicular to one another. This is because the overlap of $p$ orbitals on neighbouring rings is maximised when the rings are planar and there is no overlap when the rings are perpendicular (fig. 3.3). The bond length between the carbon atoms joining the rings is dependent on their relative orientations, and is comparable to the $C\text{--}C$ double bond length when maximum overlap occurs and lengthens to a typical $C\text{--}C$ single bond length when there is no overlap. If conjugation can occur, the molecule is less flexible as the torsional rotation of the phenyl rings is hindered and the anisotropy of the molecular shape is marginally increased.

The cores of liquid crystal molecules can have lateral substituents placed on them, typically polar groups, which can create a permanent dipole within the core and influence the polarisation effects in the condensed phase. The presence of lateral substituents can also influence the barrier between different conformers by sterically restricting rotation. Bulky lateral substituents can decrease the anisotropy of the molecular shape so small species, such as fluorine, are preferentially used as they can tailor the electronic structure of a liquid crystal molecule without significantly distorting its shape.

Two important physical characteristics of the liquid crystal molecules, which are influenced by the structure of this internal core and important in determining the phase behaviour of the molecule are the torsional potential and molecular dipole moment.
CHAPTER 3. FLUOROTERPHE NYLS

Figure 3.3: Part A shows how conjugation may arise when two phenyl rings lie in the same plane with overlap of the carbon p orbitals. Part B shows how there is no overlap of the p orbitals and consequentially no conjugation when the rings are perpendicular to one another. The shading indicates the phase of the orbitals.

The torsional energy of the molecule in this case is the energy which is required to twist two phenyl rings around a C–C bond linking them together (fig.3.4). There is often a potential barrier restricting this motion and this is known as the torsional potential. This barrier is usually of the order of 0.1 eV for small molecules without any bulky substituents which allows virtually unhindered rotation about the bond, but for larger and more complicated molecules can be large enough to separate different configurations of the molecule. As the torsional energy is typically small when compared to, for instance, the vibrational energy, this makes it difficult to determine experimentally. Also for many experimental techniques[81, 82] it is only possible to determine the torsional potentials of molecules in solution, which makes an accurate specific torsional barrier difficult to deduce. This problem is therefore suited to investigation using computer simulation. The preferred conformation of the molecule is dependent
Figure 3.4: Diagram indicating the torsional axis and dihedral angle between two phenyl rings.

on both electronic and steric effects. For instance, in biphenyl there is competition between by the delocalisation of the electrons across the entire molecule when the phenyl rings lie in the same plane, and steric repulsion between the hydrogens which would indicate that the preferred conformation would have the planes of the phenyl rings perpendicular to each other. The equilibrium angle lies between these two extremes and its exact value is determined by which effect leads to the greatest influence on the energy. When bulky substituents are added to biphenyl they effect the electronic structure, depending on whether they accept or donate electrons, but usually have a much greater effect on increasing the steric repulsion if they are placed on carbon atoms adjacent to the bond linking the rings.

This balance of electronic and steric effects on the equilibrium conformational angle is observed in biphenyl and terphenyl molecules. Studies on the
isolated biphenyl molecule [34, 83, 84, 85] find the 0° and 90° conformers (0° corresponds to the planar conformer) to be maxima on the torsional potential surface. Rumi and Zerbi [83] find the equilibrium conformational angle to be 38° with barriers of the order of 0.16eV at 0° and 0.04eV at 90° using Hartree–Fock calculations, which is in qualitative agreement with the other experimental [84] and computational [34] studies. The conformation potential surface of terphenyl determined by Rumi and Zerbi [83] is very similar with a minimum occurring when the rings are 39° to each other, but with the barrier heights approximately doubled in value to 0.31eV at 0° and 0.08eV at 90°. The torsional potential surface of one of the angles was examined while the other was fixed and was found to be similar to that of biphenyl. This suggests that the influence of one terminal phenyl ring on the other is not significant.

The presence of a permanent electric dipole in molecules occurs when the electron distribution over the molecule is not symmetric. This leads to localised partial negative and positive charges in the molecule and depends on the symmetry and constituent species of the molecule. The electric dipole can be defined by two charges, \( q^+ \) and \( q^- \), separated by a distance, \( l \), and represented by a vector directed from \( q^- \) to \( q^+ \) (although conventionally drawn in the opposite direction). The magnitude of this electric dipole is the electric dipole moment \( \mu = ql \). In these calculations the molecular electronic dipole moment is determined by determining the vector difference between the centres of positive and negative charge. The position and direction of a permanent molecular dipole are usually
determined by the position of an electronegative species or a polar bond without a symmetric equivalent. A permanent electric dipole can affect the response to and orientation of a molecule in an external electric field. In calamatic liquid crystal molecules there is a permanent molecular dipole moment when a polar group is present at one end of the molecule (fig.3.1). The effect of the terminal polar group is enhanced by the elongated shape and electron delocalisation over the molecule. It is the direction of this dipole moment and therefore the entire molecule which is aligned by the applied electric field in liquid crystal displays. The molecular dipole moment creates regions of charge accumulation and depletion within the molecule which affect the way the molecule interacts with its neighbours in the bulk material. Many aspects of liquid crystal phase behaviour can be successfully modelled by only considering the molecular dipole moment, ignoring the detail of the molecular structure.

In 2,2'-fluoro-terphenyl, the magnitude and direction of the molecular dipole moment are expected to be dependent on the conformational angles. The dipole moment calculations performed here are done on molecules with fixed geometries with different conformational angles and the temperature is fixed at 0K. Here the 0° conformer is defined as the molecule in which the two fluoride groups are next to each other (fig.3.5A). The fluoro substituted conformer shown in fig.3.5B, which is defined as having the fluoro substituents at 180° to each other, would be expected to have a molecular dipole moment in a different direction with a different magnitude to 3.5A. Where the fluoro substitutes are opposite to
each other the dipole moment would extend along the long axis of the molecule (parallel molecular dipole moment) and where they are next to each other the dipole would be across the molecule (perpendicular molecular dipole moment). However, the parallel dipole would not be expected to be as large as the perpendicular dipole. From a consideration of fluoro substituted biphenyl the dipole would be expected to be zero for the 180° conformer, so the magnitude of the parallel dipole moment is therefore largely dependent on the presence of the third phenyl ring as this breaks the symmetry of the molecule. This study aims to assess the dependence of the magnitude and direction of the molecular dipole moment on the torsional angle.

DFT as implemented in CASTEP and VASP provides a computationally economical way of performing detailed calculations on the electronic structure of molecules of this size. A study by Karpfen et al [86] has shown that the inclusion of the electron correlation interaction is an important factor in accurately describing conjugated systems; CASTEP ensures the inclusion of the correlation interaction for large molecules. The expansion of the K–S orbitals in a planewave basis set is a convenient way of including the delocalised electron structure in the calculation. The planewave DFT codes using the GGA approximation to the exchange-correlation energy have previously been shown to be capable of simulations of conjugated systems [34].

The next section details the input parameters used in this calculation and this is followed by a presentation and discussion of the results.
3.1.1 Details of the Calculations

2,2'-difluoro-terphenyl (fig.3.5) molecules were characterised using DFT as implemented in CETEP (Cambridge Edinburgh Total Energy Package, an early parallel version of CASTEP). The dipole moment of 2,2'-fluoro-terphenyl was calculated for two different conformations, one with the fluorine atoms next to each other and the other where they are opposite (2,6'-fluoro-terphenyl) to one another as shown in fig.3.5, to determine how the direction and magnitude of the dipole changes with the torsional angle.

The $q_e$ tuned Kleinman–Bylander [87] pseudopotentials were used entailing a
planewave kinetic energy cutoff of 800eV for biphenyl and 1000eV for the fluoro substituted terphenyl. The magnitude of the planewave cutoffs was determined by converging the total energy of the systems to within $10^{-4}$eV on increasing basis set size. The dimensions of the supercell were also large enough to ensure this convergence of the total energy on increasing the size of the supercell. For the dipole moment calculations it was important to ensure that there was no spillage of electron density associated with a molecule into a neighbouring supercell. For 2,2'-fluoro-terphenyl the dimensions of the supercell were $9 \times 9 \times 18\text{Å}$ ensuring a separation between neighbouring molecules of at least $5\text{Å}$, regardless of torsional angle.

The geometries and relative energies of the conformers were determined by relaxing the atomic positions according to the Hellmann–Feynman forces until no force exceed a tolerance of $0.1\text{eVÅ}^{-1}$. The starting geometries have bond lengths of C–C: $1.40\text{Å}$, C–H: $1.08\text{Å}$, C–F: $1.33\text{Å}$ with internal angles in the phenyl rings of $120^\circ$. There were no constraints placed on the relaxations of the atoms. As the relaxation of the bond lengths and angles first finds a metastable molecular configuration, convergence of the total energy to $10^{-5}\text{eV}$ is obtained. If the calculation is allowed to continue the geometry of the molecule distorts while relaxing to a lower energy conformer. The torsional potential surface is then taken by plotting the total energy as a function of torsional angle so that stable conformers and barriers to rotation may be determined.

The molecular dipole moment of 2,2'-difluoro-terphenyl is then determined
using fixed geometries for two conformers, both with the torsional angle between phenyl rings 2 and 3 fixed at $0^\circ$ with the torsional angle between phenyl rings 1 and 2 set at $0^\circ$ and $180^\circ$. This gives an indication of whether the switch in the direction of the molecular dipole occurs between longitudinal and latitudinal on changing the conformational angle. The molecular dipole moment is determined by taking the vector difference between the centroids of nuclear and electron charge distributions as defined previously.

### 3.2 Torsional Potentials of Fluoro Substituted Terphenyls

The presence of fluoro substituents on terphenyl is expected to influence the magnitude and positions of the maxima and minima on the torsional potential energy surface. A planewave DFT study comparing the torsional potentials of biphenyl and 2,2'-difluoro–biphenyl was completed by Adam et al [34]. In biphenyl this determined that there were barriers to torsional rotation at $0^\circ$ and $90^\circ$, the minimum occurred at $42^\circ$, which indicates that the equilibrium conformer involved a compromise of electronic and steric effects. The barrier at $90^\circ$ was $0.37eV$ greater than that at $0^\circ$ which suggests that the effect of conjugation had the greater influence in determining the shape of the torsional potential surface. On addition of the fluoro substituents the torsional potential surface was no longer symmetrical about $90^\circ$. The barrier to rotation for 2,2'-difluoro–biphenyl
at 0° had increased by approximately 0.3eV, the barrier at 90° had decreased by about 0.05eV and the barrier at 180° had increased by 0.09eV when compared to the 0° conformer of biphenyl. These results can be explained on consideration of the highly polarised C–F bond which allows the fluorine atoms to adopt a partial negative charge. For the 0° conformer of 2,2′- difluoro-biphenyl there is a strong repulsion between the electronegative fluorine atoms; for the 90° conformer the effect of loss of conjugation is not as pronounced as for biphenyl as the fluorine atoms reduce the electron density within the π bonds of the phenyl rings; and for the 180° conformer the effect of the repulsions between the fluorine atoms has been replaced by a weaker repulsion between fluorine and hydrogen. The barriers at 0° and 180° are therefore greater than that at 90° which indicates that steric repulsions are now prevalent over electrostatic repulsion between the fluorine atoms in the determination of the torsional potential surface.

The addition of fluorine substituents has changed the dominant effect in determining the most stable conformer from the conjugation of the electronic structure to steric repulsion. In biphenyl the barrier for the 0° conformer is approximately 0.03eV lower than that for the 90° conformer, whereas in 2,2′- difluoro-biphenyl the 90° conformer is lower in energy than the 180° conformer by about 0.13eV. Apart from indicating a stronger steric repulsion between the fluorine atoms than between a fluorine and a hydrogen atom, this also suggests a strong reduction in the delocalisation of electrons over the molecule caused by the fluorine substituents polarising and therefore localising the electron density on the
molecule so reducing conjugation.

From the behaviour of fluoro substituted biphenyl steric repulsions between the fluorine atoms would be expected to dominate rotations about $\tau_1$ whereas conjugation could be important in determining the rotation about $\tau_2$ (as defined in fig.3.5). The barrier of $\tau_2$ would be modified from that of biphenyl as the steric repulsion between fluorine and hydrogen is greater than that between two hydrogens, reducing the dominance of conjugation in determining the most stable conformation.

From an examination the general shape of the torsional potential surface
in fig.3.6 and fig.3.7, it is clear that the torsional potential changes more with respect to the value of $\tau_1$. $\tau_2$ roughly follows what would be expected from the torsional potential surface of biphenyl for each value of $\tau_1$ (for example see fig.3.8). The study on 2,2'-difluoro-terphenyl found the global minima on the torsional potential surface (fig.3.6) occur when $\tau_1$ is 65° and $\tau_2$ is 33°; $\tau_1$ is 65° and $\tau_2$ is 147°, when $\tau_1$ is 106° and $\tau_2$ is 33° (visible in fig.3.7). These indeed conform to expectations in that $\tau_1$ allows the fluorine atoms to move away from each other whereas $\tau_2$ allows the phenyl rings to be closer to planarity so increasing electron conjugation. The maximum occurs when $\tau_1$ is 0° and $\tau_2$ is 90°
Figure 3.8: The torsional potential surface for $\tau_2$ when $\tau_1$ is kept fixed at 0°. with a local maximum at $\tau_1$ at 180° and $\tau_2$ at 90° which agree with prediction based on the 2,2'-difluoro-biphenyl study. There is also a local maximum which occurs when $\tau_1$ is 90° and $\tau_2$ is 90° where the terminal phenyl rings are almost perpendicular to the central ring. The difference in energy between the lowest energy conformer and the highest energy conformer is approximately 0.67eV. As previously stated, the equilibrium value of $\tau_1$ is influenced more by steric and electrostatic repulsions between the fluorine atoms than by electron conjugation.
For each value of $\tau_1$ the torsional potential of $\tau_2$ follows a path as would be expected for the torsional potential of biphenyl (fig.3.8).

Parallels can be drawn between comparisons of 2-2'-difluoro-biphenyl [34] with 2-2'-difluoro-terphenyl [83] and biphenyl with terphenyl [83]. In both cases the influence of the additional phenyl ring is mainly to increase the torsional barrier heights (0.41 eV for 2-2'-difluoro-biphenyl and 0.67 eV for 2-2'-difluoro-terphenyl, 0.31 eV for biphenyl and 0.16 eV for terphenyl), but does not change the positions of the minima or maxima by a significant amount (positions of minima: 60° in 2-2'-difluoro-biphenyl and 65° for $\tau_1$ in 2-2'-difluoro-terphenyl, 38° in biphenyl and 39° for $\tau_1$ in terphenyl). Also the addition of the fluoro substituents to terphenyl has a similar effect to their addition to biphenyl: the symmetry of the torsional potential surface is broken about 90° in terphenyl with an increase in the barrier heights at 0° (see above) in a similar manner to the biphenyl case. In these respects the torsional potential surface of 2-2'-difluoro-terphenyl is what would be expected on consideration of these previous studies.

The bond lengths within the molecule are expected to alter on changing the conformational angle. In particular the lengths of the bridging C–C bonds are expected to increase as the conformer is distorted away from planarity. This is due to a decrease in the overlap of the carbon $p$ orbitals which results in a loss of conjugation and consequentially a weakening of the bond. Indeed when $\tau_1$ is 90° the bond distance increases to 1.46 Å compared to a distance of 1.43Å when $\tau_1$ is 0°. Also there are strong forces pushing the C–F bonds out of the plane
of the phenyl rings when \( \tau_1 \) is 0° and 180° due to steric repulsion between the fluorine atoms or a fluorine atom with a hydrogen.

### 3.3 Molecular Dipole Moment of 2,2'-difluoro-terphenyl

The changes in the direction of the molecular dipole moment for different conformational angles are presented in table 3.1 and fig.3.9. These results show that when \( \tau_1 \) is 0° the dipole is directed towards the side of the molecule on which the fluorine substituents are located. On positioning the fluorines ortho to one another, the dipole moments directed towards the end of the molecule where the electronegative fluorine atoms have a significant influence on the electron distribution. There is therefore a detectable dipole moment along the long axis of the molecule (parallel molecular dipole moment). Even when \( \tau_1 \) is 180° there is still a significant lateral dipole moment though, but in the opposite direction across the molecule to that of the 0° conformer. This would suggest that the C–F bond on the first ring is much more polarised than that on the second. This would be expected as the third phenyl ring could provide charge density which decreases the charge density difference within the C–F bond. A Mulliken population analysis determined that the overlap population of the C–F bond on the first ring was 0.47e and that on the second was 0.46e. However, the charges on both of the fluorine atoms was identical at -0.34e as were the charges on the
### Table 3.1: Dependence of direction and magnitude of molecular dipole moment on conformational angle for 2,2'-difluoro-terphenyl. The D refers to Debyes. Y and Z refer to components along the respective axes as shown in fig.3.4 and the numbers in the table refer to the proportion of the dipole moment in the specified direction.

<table>
<thead>
<tr>
<th>Conformer</th>
<th>Molecular Dipole Moment /D</th>
<th>Y</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>0°</td>
<td>1.9</td>
<td>1.0</td>
<td>0.0</td>
</tr>
<tr>
<td>180°</td>
<td>1.4</td>
<td>-0.6</td>
<td>0.8</td>
</tr>
</tbody>
</table>

The molecule remains mainly at the lowest energy conformation, in this case where $\tau_1$ is 65° and $\tau_2$ is either 33° or 147° and where $\tau_1$ is 106° and $\tau_2$ is 33° and so the average dipole moment of the molecules is that which occurs for these low energy conformers. The proportion of different conformers in a sample varies as a function of temperature. As the temperature is increased it is possible that the torsional barrier may be overcome, but the molecule will still spend most of its time in its lowest energy conformation. The average molecular dipole moment is dependent on its value for the average conformational angle which varies with the temperature, but will be dominated by the value of the molecular dipole moment at the lowest energy angle. The longitudinal dipole moment occurs at a local maximum on the torsional potential surface and so due to the instability of the conformer is unlikely to have a strong influence on the phase behaviour of the liquid crystal with this mesogen at its core. Also as there is a significant perpendicular component to the dipole moment in this conformer, lateral interactions between molecules could still predominate in explaining the phase behaviour. In a study of the phase behaviour of the liquid crystals with cores shown in fig.3.10...
[88], the lateral interactions between molecules due the situation of the fluorine substituents explains the tilt angle in the smectic C phase. The anomalous behaviour reported where the tilt decreases with decreasing temperature can be explained as being due to the enhanced lateral association between molecules.

So the dependence of the direction of the molecular dipole moment in 2,2'-difluoro-terphenyl on the conformational angle exists, where a significant longitudinal molecular dipole moment arises on changing the rotational angle. On consideration of the study by Loubser [88] the intermolecular interactions are more likely to have the strongest influence in determining the preferred conformational angle than consideration of intra molecular steric repulsions and electron conjugation. This would suggest that liquid crystal molecules containing fluoro substituted biphenyl or terphenyl groups at their core would display similar phase behaviour, the dominant factor being lateral interactions between molecules caused by the presence of highly polar C-F bonds. However, the results of this study indicate that the magnitude and direction of the molecular dipole moment are dependent on the conformational angles, which would result in different alignments of the molecules at different temperatures.
Figure 3.9: Diagram showing the rough dependence of the molecular dipole moment in the $y$ and $z$ directions on the torsional angle. The dipole along the $y$ direction shows how this decreases as the dipole along the $z$ direction increases and then increases in magnitude again but in the opposite direction. This is because the fluorine atom on the central benzene ring is more electronegative than that on the terminal benzene ring and so the dipole moments due to the fluorine atoms in the $y$ direction do not cancel each other at $180^\circ$ as they do for the fluoro substituted biphenyl equivalent.
Figure 3.10: Diagram showing part of the core of the SO-4-n-octyloxydifluorbiphenyl-4'-yl 3-fluoro-4-(2-fluoroctyloxy)-benzoate liquid crystal molecules studied by Loubser et al [88]. Either $X_1=F$ and $X_2=H$, or $X_1=H$ and $X_2=F$. 
Chapter 4

Ethylene and Aluminium

4.1 Introduction

A description of conjugated molecules on $s-p$ metal surfaces is essential for an understanding of a range of adsorption processes. For instance, the contact between organic films and the contact metal in organometallic devices where a knowledge of the behaviour of electrons in the system can lead to the tailoring of systems for specific functions. In particular an investigation into the combining of the $\pi$ molecular orbitals of organic molecules with metallic $s-p$ bands can lead to a characterisation of the nature of the binding between the species and the strength of this interaction. Previous studies have concentrated on the adsorption of organic molecules to transition metal surfaces [1, 89, 10, 90], where the metallic $d$ band is thought to dominate the nature of the adsorption process. Therefore the role played by the $s-p$ band in the binding of adsorbates, if any, is
poorly understood. The ethylene/aluminium system provides an uncomplicated example of this interaction as it is highly unlikely that the unoccupied d-orbitals would be involved in any binding interaction, being of too great an energy.

The adsorption of benzene on Al(111) has been investigated by Duschek et al [37] using angle-resolved ultraviolet photoelectron spectroscopy (ARUPS), high-resolution electron energy loss spectroscopy (HREELS), thermal desorption spectroscopy (TDS) and a DFT computer simulation using the VASP code. This determined that benzene lay with its molecular plane parallel to the surface at a distance of 3.7Å above the surface and that only a weak electrostatic interaction between the species could be discerned. However, in studies investigating Al(C$_6$H$_6$) it has been found that the aluminium atom was chemically bound to the benzene molecule [91, 92, 93]. Studies investigating the adsorption of ethylene on aluminium have concentrated on characterising the Al(C$_2$H$_4$) and [Al(C$_2$H$_4$)]$^+$ complexes and are reviewed in detail in section 3.3. In each study the Al atom is symmetrically bound above the centre of the C–C bond. In a CASTEP study of ethylene on Al(111) by Zhou et al [39] it was proposed that each carbon atom in ethylene formed a separate bond with a different aluminium atom. There is therefore some dispute over how ethylene binds to an extended aluminium surface and why the organic π molecular orbital forms a bonding combination with the p orbitals on an isolated aluminium atom but benzene is only physisorbed on an extended metal surface.

Initially the isolated Al(C$_2$H$_4$) and [Al(C$_2$H$_4$)]$^+$ complexes are investigated to
compare the results presented here with previous studies, then the adsorption of an isolated \( \text{C}_2\text{H}_4 \) molecule on a Al(100) slab is simulated. The advantage of using planewave DFT codes is that a planewave basis set can be used in characterising both systems. The results therefore determine not only the nature of the adsorption interaction, but also how valid it is to assume that adsorption on a \( s-p \) metal is a localised interaction. In this chapter the conclusions from both the molecule and slab calculations are used in explaining the behaviour of ethylene at an aluminium surface.

The details of the calculations specific to the ethylene/aluminium systems are presented in section 4.2. The Al(\( \text{C}_2\text{H}_4 \)) and [Al(\( \text{C}_2\text{H}_4 \))]\(^+\) calculations are detailed in section 4.3 and a characterisation of the isolated Al(100) slab is presented in 4.4. The results from the investigation into adsorption on an extended slab are presented in 4.5 and the conclusions are discussed in section 4.6.

4.2 Details of the Calculations

The Density Functional Theory (DFT) of Hohenberg and Kohn [63] was implemented using the CASTEP and CETEP codes (Cambridge–Edinburgh Total Energy Package) [21] as explained in chapter 2. The GGA [65, 25] approximation for the exchange-correlation interaction was used and the GGS [65, 25] spin polarised approximation was required for the Al(\( \text{C}_2\text{H}_4 \)) calculations. In this computation the Kohn–Sham (KS) orbitals [64] are used to describe the valence
CHAPTER 4. ETHYLENE AND ALUMINIUM

The pseudopotentials of Kleinman–Bylander are implemented. The KS orbitals are expanded using a basis set of planewaves taken up to a specified kinetic energy cutoff of 700 eV for all \((C_2H_4)/Al\) calculations and 250 eV for calculations involving only aluminium, the basis set being checked for completeness by the convergence of the total energy of the system as the cutoff is increased (a calculation on Al with a 250 eV cutoff gives the same result as that with a 700 eV cutoff). The energy is minimised using the method of steepest descents until the energy has converged to within \(2 \times 10^{-4} \) eV. The nuclei are moved under the influence of Hellmann–Feynman forces once the ground state electronic structure has been determined until the force acting on each ion does not exceed a certain tolerance, here taken to be 0.05 eV Å\(^{-1}\).

In order to characterise the binding between ethylene and aluminium, calculations were done on five systems: the isolated complexes Al\((C_2H_4)\) and [Al\((C_2H_4)\)]\(^+\), the Al\((100)\) surface, ethylene adsorbed at both top and bridge sites on a fixed Al\((100)\) surface (fig.4.1), and a larger calculation where the top surface layers were allowed to relax in response to the adsorption of ethylene. The contents of the supercells is shown in fig.4.2. For the calculations involving the Al\(^+\) ion, a uniform background negative charge is included to counteract the infinite positive charge generated by the ions in all the supercells.

For the calculations on the complexes, a supercell of dimensions 8\(\times\)8\(\times\)8 Å was required to isolate the molecules (the total energy of the system decreased by 0.0073 eV on going from a 7\(\times\)7\(\times\)7 Å to a 8\(\times\)8\(\times\)8 Å cell and by 0.0006 eV on
Figure 4.1: Diagram showing the top and bridge sites of ethylene on Al(100). The blue circles represent aluminium atoms in the top layer and the red circles represent atoms in the second layer.

Going from a $8 \times 8 \times 8\text{Å}$ to a $9 \times 9 \times 9\text{Å}$ cell). For the isolated aluminium surface the slab was separated from the slabs in supercells above and below by a vacuum region of $5\text{Å}$, the total energy having been checked for convergence with respect to vacuum depth. For convergence of the total energy, five layers of aluminium were needed with the geometry of the top two layers allowed to relax and the bottom three were kept fixed in the bulk geometry. As the surface relaxation of Al(100) has been reported to be less than 1% [94, 95, 96, 97], adsorption calculations were performed with an isolated ethylene molecule being adsorbed onto a two layer fixed slab. For the convergence of the total energy, the slab had to have dimensions of $2 \times 2$ unit cells (approximately $8 \times 8\text{Å}$) in the surface plane in order to separate the ethylene molecules. In the final calculation ethylene was positioned at the top site above a slab of 5 layers in which the geometry of the lower three were fixed and dimensions of $2 \times 2$ unit cells in the surface plane.
Figure 4.2: Contents of the supercells for calculations on Al(C$_2$H$_4$)(fig.4.2A) and C$_2$H$_4$ at a top site on a two layer fixed slab of Al(100)(fig.4.2B). Calculations on [Al(C$_2$H$_4$)]$^+$ had a similar starting configuration to A and all the adsorption calculations had a similar starting configuration to B.

There was at least 5Å of vacuum separating the ethylene molecule from the slab in the cell above it in both adsorption calculations.

A plausible starting geometry of the system was placed in the supercell, and the total energy of other possible structures was compared to the final configuration to ensure that we had determined the ground state structure. For the Al(C$_2$H$_4$) and [Al(C$_2$H$_4$)]$^+$ calculations this involved looking at different positions of Al relative to the ethylene molecule, for example with the aluminium at different heights over a carbon atom. It was found that in all cases when the geometry of the molecule was relaxed, the position of the aluminium moved towards the centre of the C–C bond. For the adsorption calculation the initial adsorbate-substrate distance was varied between 2Å, corresponding to the length of a covalent bond, and 4Å at which no attraction between the species is detected.
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For the isolated molecule calculations the states are determined at one k-point, the Γ point of the supercell. For calculations performed on metallic slabs which are finite and therefore aperiodic in one direction, the states need only be determined using a two dimensional k-point grid. For the isolated surface a grid of 13x13x1 with 28 special points was required, for C₂H₄ on 2 layers of Al(100) and C₂H₄ on 5 layers of Al(100) a 4x4x1 with 4 special points determined according to the scheme of Monkhorst–Pack [66].

The binding energies of the complexes were determined by subtracting the total energies of the isolated aluminium atom or ion and the isolated ethylene molecule from the total energy of the complex. The adsorption binding energies are calculated by subtracting the energies of the isolated adsorbate molecule and the isolated aluminium slab from the total energy of the adsorption system.

4.3 Al(C₂H₄) and [Al(C₂H₄)]⁺

Previous studies have concentrated on the bonding within the Al(C₂H₄) and [Al(C₂H₄)]⁺ complexes [98, 99, 100, 101, 102, 103, 104], extending their conclusions to bonding schemes for chemisorption on an aluminium surface. The proposed binding schemes are illustrated in fig.4.3. It is agreed that a chemical bond is formed between the two species but the nature of this bond and the manner of electron transfer is disputed. Despite this disagreement, all studies agree that Al(C₂H₄) is a stable complex with the aluminium symmetrically above the
Figure 4.3: Five previously suggested bonding schemes for Al(C_2H_4). Scheme 4.3d was favoured in an electron spin resonance (ESR) study by Kasai [98], whereas scheme 4.3c was favoured in a study by Manceron et al [100] using fourier transform infra red (FTIR) spectroscopy and post Hartree-Fock calculations. A DFT study by Alikhani et al [101] using localised basis sets identified 4.3e as the most favourable scheme by using an electron localisation function (ELF) analysis of the charge density surface.

Centre of the C-C bond. The previous studies on [Al(C_2H_4)]^+ also state that the symmetrically bound complex is the most stable. An ab-initio Hartree-Fock and DFT study by Stöckigt [103] suggested a binding scheme where the strongest interaction is a σ donation from the C-C π bond into an empty Al 3p orbital.

The calculations presented here predict that Al(C_2H_4) and [Al(C_2H_4)]^+ are stable symmetrically bound complexes. The binding energies given in table 4.1 compare favourably with experimental and indicate that a chemical bond is formed between ethylene and aluminium. For Al(C_2H_4) the value is 0.382 eV above the experimental lower bound set by Mitchell [99] and for [Al(C_2H_4)]^+ the
CHAPTER 4. ETHYLENE AND ALUMINIUM

<table>
<thead>
<tr>
<th>Study</th>
<th>C−C/Å</th>
<th>C−H/Å</th>
<th>Al Height /Å</th>
<th>Binding Energy /eV</th>
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<tr>
<td>( \text{C}_2\text{H}_4 )</td>
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<tr>
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<td>1.513</td>
<td>1.093</td>
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<td>Stöckigt [103] ( \text{[Al(C}_2\text{H}_4)]^+ )</td>
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<td>( \text{[Al(C}_2\text{H}_4)]^+ )</td>
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<td>1.088</td>
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<td>0.784</td>
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<td>Alikhani [101] ( \text{Al(C}_2\text{H}_4) )</td>
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<td>1.080</td>
<td>2.182</td>
<td>0.577</td>
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<tr>
<td>( \text{Al(C}_2\text{H}_4) )</td>
<td>1.391</td>
<td>1.086</td>
<td>2.111</td>
<td>1.076</td>
</tr>
</tbody>
</table>

Table 4.1: Results of the \( \text{Al(C}_2\text{H}_4) \) and \( \text{[Al(C}_2\text{H}_4)]^+ \) calculations compared to previous calculations. By comparing the C−C and C−H bond lengths of \( \text{C}_2\text{H}_4 \) in \( \text{Al(C}_2\text{H}_4) \) and \( \text{[Al(C}_2\text{H}_4)]^+ \) with isolated \( \text{C}_2\text{H}_4 \) and \( \text{C}_2\text{H}_6 \), an estimate can be made on how much \( \pi \) character in the organic molecule is lost on complexation. The height of Al above the plane of the molecule and the binding energy indicate the formation of a chemical bond between the species. The results compare favourably with the other studies listed.

value is 0.134 eV above the value determined by Stöckigt [103] using post HF calculations. The calculated ground state geometries are illustrated in fig.4.3. The lengthening of the C−C bond in both complexes compared to gas phase ethylene (shown in table 4.1), and the bending of the C−H bonds out of the molecular plane (shown in fig.4.4), suggest a loss of \( \pi \) character of the C−C bond in ethylene. This indicates that there is electron transfer from the C−C \( \pi \) bond to aluminium and also occupation of the ethylene \( \pi^* \) molecular orbital. This is supported by the charge density plot of the binding K−S orbitals shown in fig.4.5. \( \text{[Al(C}_2\text{H}_4)]^+ \) is bound by a \( \sigma \) interaction and is illustrated in fig.4.5. The Mulliken population analysis gives Al a charge of 0.88e which compares favourably to values of 0.87e in \( \text{[Al(C}_5\text{H}_5)]^+ \) determined by Stöckigt [92]. As the positive charge normally associated with Al has been reduced from 1.0, the interaction must involve charge transfer as some electron density must be redistributed over the molecule and onto the metal atom. This indicates a
Figure 4.4: The ground state equilibrium geometries of Al(C₂H₄) and [Al(C₂H₄)]⁺
Figure 4.5: The charge density surface of the K–S orbital corresponding to the \( \sigma \) interaction (4.5a). The charge density shown is that for \([\text{Al}(\text{C}_2\text{H}_4)]^+\). The charge density surface of the K–S orbital corresponding to the \( \pi \) interaction in \( \text{Al}(\text{C}_2\text{H}_4) \) (4.5b).

Transfer of electrons from the \( \pi \) bonding molecular orbital of ethylene to an unoccupied \( p \) orbital on \( \text{Al}^+ \) and is consistent with a \( \sigma \) interaction.

In \( \text{Al}(\text{C}_2\text{H}_4) \) the \( \sigma \) bond illustrated in fig.4.5 is dominant according to the energy level diagram showing the eigenvalues of the K–S orbitals in fig.4.6 with additional binding from the \( \pi \) interaction illustrated in fig.4.5. The Mulliken population analysis gives Al a charge of 0.46e which indicates that there is a transfer of electron density from Al to \( \text{C}_2\text{H}_4 \) as in the \( \sigma \) interaction where there is donation from the \( \text{C}_2\text{H}_4 \) binding \( \pi \) molecular orbital to an unoccupied Al \( p \)
orbital. However, when compared to the value of 0.88e in $[\text{Al(C}_2\text{H}_4)]^+$, there must be significant back donation via the $\pi$ bond illustrated in fig.4.6. This occurs by a transfer of electron density from the occupied Al $p$ orbital into the empty $\text{C}_2\text{H}_4 \, \pi^*$ orbital.

The calculations therefore indicate that the $\sigma$ interaction involving donation from the $\text{C}_2\text{H}_4 \, \pi$ molecular orbital into an empty Al $p$ orbital is dominant in both complexes. The donation of electron density from the $\text{C}_2\text{H}_4 \, \pi$ molecular orbital and the back donation in $\text{Al(C}_2\text{H}_4)$ indicate that the C-C bond loses its $\pi$ character on bonding with aluminium. Scheme d in fig.4.3 proposed by the ESR study of Kasai [98] is in close agreement with this conclusion.

4.4 Al(100)

The calculated bulk lattice parameter of aluminium of 3.95Å compares favourably with the crystal structure value of 4.05Å [105]. The calculation of the Al(100) surface structure determined that only the top two layers were displaced in the direction perpendicular to the surface plane with no movement of atoms within the plane. This agrees with previous experimental studies [95, 96, 106] and calculations [97]. The surface contraction was 0.6% between these two layers, the spacing between surface layers differing from that between bulk layers by 0.01Å. This is to be expected as the uppermost layer moves closer to the bulk in order to increase the co-ordination of its atoms and stabilise the surface. The
Figure 4.6: The energy level diagram for the binding interactions in Al(C₂H₄) and [Al(C₂H₄)]⁺. Although the energy values are not considered to be absolute, the diagram gives a qualitative picture of the comparative strengths of the different interactions. Here it can be seen that a stabilising σ interaction in the complexes is dominant as the Al pₓ and C₂H₄ π orbitals combine to form a lower energy molecular orbital. The Al pₓ and C₂H₄ π* combine to form a lower energy π molecular orbital in the Al(C₂H₄) complex.
surface energy was found to be 0.480eV per atom with a difference from the surface energy of the terminated bulk structure of only 0.0002eV per atom. The stability of the (100) surface could due to the similarity between the bulk structure and this open surface plane, so there is little relaxation and certainly no reconstruction of the surface layer. The (011) and (111) surface planes of aluminium experience a greater relaxation, the (111) surface expands by as much as 3.1% according to an LEED study by Martinez et al [107] and the (011) surface contracts by as much as 8% but without reconstruction according to an LEED study by Norman et al [108].

4.5 \( \text{C}_2\text{H}_4 \) on Al(100)

The calculations for adsorption on a fixed slab show that ethylene lies with its molecular plane parallel to the surface plane and retains its gas phase geometry when adsorbed at top and bridge sites on Al(100) (table 4.2). The binding energy and height of \( \text{C}_2\text{H}_4 \) above Al(100) (table 4.2) suggest a very weak interaction but the top site is preferred over the bridge site. In the DOS plot for adsorption at a top site shown in fig.4.7 six sharp peaks can be identified corresponding to the six ethylene molecular orbitals which also indicates that ethylene retains its molecular identity. A Mulliken population analysis (table 4.3) showing there to be no charge transfer, and the charge density surface shown in fig.4.9 in which no build up of charge density between the species can be discerned, is
Table 4.2: The geometry of ethylene, the binding energies and perpendicular distance between molecule and surface for ethylene adsorbed on a fixed slab of Al(100). If the C–C and C–H bond lengths are compared with the values for ethylene in table 4.1 it can be seen that ethylene retains its molecular geometry on adsorption. The binding energy is an order of magnitude less than in the complex molecule and the C₂H₄–Al distance about 0.8Å greater than the corresponding values for the complexes shown in table 4.1. This would suggest a much weaker interaction than that acting to bind the complexes.

<table>
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<th>System</th>
<th>C–C/Å</th>
<th>C–H/Å</th>
<th>Binding Energy /eV</th>
<th>Height of C₂H₄ /Å</th>
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<tr>
<td>Top Site</td>
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<td>1.086</td>
<td>0.0345</td>
<td>3.505</td>
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<tr>
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<td>1.315</td>
<td>1.087</td>
<td>0.0206</td>
<td>3.507</td>
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Table 4.3: The Mulliken population analysis for ethylene adsorbed at a top site on Al(100). No charge transfer can be discerned between the ethylene molecule and the aluminium surface. The aluminium atom below the centre of the C–C bond does gain a positive charge which suggests that an electrostatic interaction is possible.

<table>
<thead>
<tr>
<th>Atomic Species</th>
<th>Charge /e</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>-0.54</td>
</tr>
<tr>
<td>H</td>
<td>0.27</td>
</tr>
<tr>
<td>Al (beneath C–C)</td>
<td>0.03</td>
</tr>
<tr>
<td>Al (top layer)</td>
<td>-0.01</td>
</tr>
<tr>
<td>Al (bottom layer)</td>
<td>0.00</td>
</tr>
</tbody>
</table>

also consistent with a weak electrostatic interaction. The forces acting on the atoms in the fixed slab are all below 0.04eVÅ⁻¹. The direction of the forces suggest that if the surface were to relax the Al atoms would move only in the surface plane and away from the ethylene molecule, apart from the Al atom which remains directly below the centre of the C–C bond.

The calculation in which the top two layers of the Al(100) surface were allowed to relax determined a height 3.5Å of ethylene above the surface, in agreement with the fixed slab calculations. Again the ethylene lies flat on the surface and no distortion of the surface in response to the presence of ethylene.
Figure 4.7: The DOS plot for ethylene adsorbed at a top site on a fixed slab of Al(100) where six peaks corresponding to the ethylene molecular orbitals can be discerned.
Figure 4.8: The charge density surface of ethylene at a top site on Al(100). No build up of charge density between the molecule and the substrate can be observed.
was observed. As the system is relaxed, the atoms below the ethylene molecule do not respond to its presence and the ethylene molecule moves away from the surface. The aluminium atom directly below the C–C bond does not move upwards to form a bond with ethylene.

Both calculations, on a fixed and relaxed Al(100) slab, indicate that ethylene is weakly physisorbed on the surface.

4.6 Discussion

The chemical binding within the complex molecules would suggest that chemisorption would take place on the extended aluminium surface. The agreement of the results for the complexes with previous studies (table 4.1) gives credence to these results. The limited relaxation of the Al(100) surface also agrees with previous experimental results. Therefore despite the lack of relevant information on the adsorption system, the planewave DFT calculations are accurate in describing features of ethylene/aluminium systems.

The adsorption calculations for the extended surface predict a physisorption interaction with probably a low energy barrier to diffusion across the surface. This disagrees with the molecular calculations which predict chemisorption. However, this apparent contradiction can be understood as the directional $p$ orbitals required to form chemical bonds in the complex molecules are not defined in the band structure description appropriate for the electronic structure
of the aluminium surface (see refs. [109, 110, 111]. A lowering of the energy of the electrons in the metal is obtained by their delocalisation over the metal, this makes the isolation of a $p$ orbital on one aluminium atom unlikely. As a chemical bond is formed in the presence of $p$ orbitals of the correct energy and symmetry, no bond is formed with the metal surface. Al(100) is an open face of fcc aluminium and therefore the most likely to have an available localised bonding site. It would therefore be expected that ethylene would physisorb at other crystal faces. However, a different scheme whereby a chemical bond could be formed between the ethylene carbon atoms and two Al atoms could be possible provided the distance between the aluminium atoms was close to that of the C–C bond length. This would result in a chemisorption interaction. This scheme has been proposed by Zhou et al [39] for ethylene on the Al(111) surface.

The adsorption of conjugated organic molecules on most transition metal surfaces is described by the Dewar–Chatt–Duncanson [112, 113] donor–acceptor model. In this model there is electron donation from the molecular $\pi$ orbitals into the empty metal $d$ orbitals and back donation from the $d$-orbitals into the molecular $\pi^*$ orbitals. It would appear from the results that a similar interaction occurs in the complex, except that here the metal $p$ orbitals of the correct symmetry are involved instead of the $d$ orbitals.

However, the metal $s$–$p$ bands used to describe the electronic structure of the surface are more diffuse than the $d$ bands which can have localised character. Therefore the Dewar–Chatt–Duncanson mechanism is unlikely to occur at an $s$–
CHAPTER 4. ETHYLENE AND ALUMINIUM

$p$ metal surface and this has indeed been shown by the work of Duschek et al.\cite{37} on benzene on Al(111). The similarity between the adsorption characteristics of benzene and ethylene on aluminium indicate that physisorption may occur for all non-polar conjugated organic molecules on the (100) face of $s$–$p$ metals. The case for organic molecules with polar substituents is somewhat different though with a binding interaction usually occurring between the polar group and the substrate.

This study also highlights the pitfalls of assuming that adsorption is a localised process. Although the characterisation of the complex molecule is accurate, the extension of the conclusions to a characterisation of an adsorption process in this case has been shown to be presumptuous. When the electronic structure of the extended metal surface is ignored, the conclusions drawn from studying reduced systems can often be misleading. If experimental studies indicate that chemisorption takes place at a specific site then the description of bonding from calculations of complexes is often accurate and straightforward. However, in this case where experimental knowledge about the system is limited, the qualitative differences in results from molecule and slab calculations show that it is not sufficient to approach the problem in an identical fashion to other similar systems.
Chapter 5

Ethylene and Copper

5.1 Introduction

The ethylene/copper system is of interest in applications such as catalysis, thin film technology and organometallic chemistry. Copper is a widely used catalyst for reactions involving unsaturated organic molecules and this study gives insight into the interactions that can occur between small intermediates, such as ethylene, and the substrate. The use of a small scale system to characterise the salient features of an adsorption interaction which involves complex adsorbates can make the identification of potentially important features in the complete system more straightforward. For thin film technology it is important to know the strength of interaction between an organic molecule and a potential substrate, the orientation of unsaturated organic molecules on the surface, and the extent of distortion of both species on adsorption is relevant in identifying suitable metal-
lic substrates. Copper is an important element in many biological compounds such as metalloproteins and enzymes. Therefore the nature of binding between the unsaturated organic ligand and the metal atom in the complex determined by computational calculations is of interest. The C–C π bond is often influential in larger scale organic molecules in determining the type of interaction with a metal. Studying ethylene therefore provides a model for explaining the interactions of copper with more complicated organic molecules. The above mentioned examples illustrate value of clearly defining the interaction between copper and ethylene; the nature of which, despite extensive experiments and simulations, is still under debate. Different possibilities for the binding of ethylene to a single copper atom are discussed at the beginning of section 5.3.1 and the different proposals for the binding of ethylene to a copper surface are discussed at the beginning of section 5.3.4.

The characterisation of the ground state adsorption configuration of ethylene on Cu(100) provides an inroad to understanding how C–C π bonds associate with a transition metal d band. The approach to this problem is firstly to perform calculations on Cu(C₂H₄) in order to identify and characterise chemical binding interactions, then characterise Cu(100) with a slab calculation, and finally to compare different adsorption sites for ethylene on a Cu(100) slab. Although experimental and computational studies have been carried out on Cu(C₂H₄) [114, 115, 116, 117, 118, 119] and C₂H₄ adsorbed on different crystal faces of copper [40, 41, 17, 42, 120, 16, 121], there is still disagreement on the nature
of the binding and the extent of localisation of the interaction between \( \text{C}_2\text{H}_4 \) and the surface. It has been assumed in many studies that the adsorption interaction can accurately be represented by a single complex [18], but a recent study by Watson et al. [120] of \( \text{C}_2\text{H}_4 \) on Cu(111) determined that a complete description of the electronic structure of the extended substrate was important to determine the nature of adsorption. This was a planewave DFT slab calculation which stated that if a low k-point density was used chemisorption occurred, but on increasing the number of k-points, and therefore the accuracy of the electronic structure of the surface, a physisorption interaction occurred. Although molecular representations are considered to be accurate for characterising highly localised chemisorption interactions, inclusion of a full description of the surface may be different to the conclusion from a study on a simplified system.

The structure of ethylene has already been outlined in the previous chapter. The copper atom may be expected to have a \( 3d^94s^2 \) arrangement of valence electrons but in fact has a \( 3d^{10}4s^1 \) arrangement in the ground state. This allows the contraction of the \( d \) orbitals and a lowering of the energy of the \( d \) electrons. As the \( d \) orbitals are poorly screening, the atom is small compared to group I elements and the first ionization energy is comparatively high. This means that copper is a noble metal and not very reactive. The favoured oxidation state in complexes is II, though I exists in some compounds. In this study it is only the neutral copper atom which is considered.

The ability of transition metals to form complexes with organic molecules is
facilitated by the presence of metallic $d$ orbitals. The weakly bound $d$ electrons not only allow ease of electron donation to acceptor ligands, but also allow flexibility in the distribution of the charge density as a result of the angular variations in their shape. The different symmetries of the $d$ orbitals permit covalent interactions with the molecular orbitals of the ligand. This may result in chelation where a ligand is able to form two bonds with the metal atom and so create a ring. As copper is a noble metal with a filled $d$ shell, it is not obvious how it should interact with organic ligands.

The most important feature of the band structure in determining the properties of fcc copper is the contracted $d$ band [122, 123]. The $d$ band has more local character than the diffuse $s$–$p$ bands, and in some cases bonds can be considered as localised between $d$ orbitals on neighbouring metal atoms. This localisation can be used to explain some of the strong chemisorption interactions on transition metal surfaces. As the $d$ band is full in copper, or almost full depending on its environment, there are electrons in states near the Fermi level which explains its high conductance, but also suggests that only weak chemisorption interactions can take place. This is because there is less opportunity for back donation where electrons are donated from the adsorbate to the metal. It would be expected that a chemisorption interaction would be more likely to take place on a corrugated surface plane, such as the (100) surface.

From an examination of the charge density surface associated with the K–S orbitals, the importance in the interaction of the closed shell copper $d$ orbitals
in binding with $\text{C}_2\text{H}_4$ may be assessed. If a chemisorption interaction occurs in the slab calculation, then it is likely that the binding characteristics are similar to those within the complex.

The next section of this chapter deals with the details of the calculations. This is followed by the results and a discussion on the bonding within $\text{Cu}(\text{C}_2\text{H}_4)$, then a characterisation of the $\text{Cu}(100)$ surface and the determination of the adsorption of $\text{C}_2\text{H}_4$ on $\text{Cu}(100)$ are presented. Finally a discussion on how the results from the complex molecule calculations explain the results from the slab calculations is given.

## 5.2 Details of the Calculations

The complex molecule $\text{Cu}(\text{C}_2\text{H}_4)$, the $\text{Cu}(100)$ surface and the adsorption of $\text{C}_2\text{H}_4$ on $\text{Cu}(100)$ were characterised in order to determine the nature of the adsorption of ethylene on copper. This was done using Density Functional Theory as implemented in the VASP code using ultra-soft Vanderbilt [68] pseudopotentials. The general gradient approximation [65] was used for the exchange–correlation interaction. The planewave kinetic energy cutoffs were taken to be 350eV for all calculations to ensure that the total energy had converged to within $10^{-4}$eV on increasing basis set size. The spin dependent general gradient approximation was implemented in the code.

$\text{Cu}(\text{C}_2\text{H}_4)$ was isolated in a supercell of dimensions $11 \times 11 \times 11 \text{Å}$ and the
supercell contents are shown in fig.5.1. The supercell dimensions were considered sufficient as an increase in the dimensions from $10 \times 10 \times 10\text{Å}$ to $11 \times 11 \times 11\text{Å}$ resulted in an increase of the total energy by 0.0057eV whereas on going from $11 \times 11 \times 11\text{Å}$ to $12 \times 12 \times 12\text{Å}$ increased the total energy by 0.0002eV. The lattice parameter of fcc copper was determined by relaxing the dimensions of a single cubic unit cell, containing 4 atoms. The starting lattice parameter was taken as 3.681Å from [105] which relaxed to 3.648Å. This calculated value was used for determining the initial geometries for the slab calculations. The Cu(100) surface was characterised using a slab in which all atomic positions were allowed to relax, therefore both surfaces were relaxed as shown in fig.2.3. The width of slab required was determined using a $1 \times 1$ cubic unit cell slab made deep enough to ensure that the spacing between the central layers had converged on increasing slab thickness and was close to the bulk inter layer spacing. This was achieved when 7 layers (14 atoms) were used where the interlayer spacing between the central layers was 1.810Å compared to the equivalent bulk spacing of 1.824Å. Only five layers, with a gap of 1.847Å between the central layers, were used for the adsorption calculations in order to make the calculations tractable. The surface was then extended to make the supercell $2 \times 2$ unit cells in the surface plane in order that the cell was large enough to accommodate an adsorbate. The ethylene molecule was then introduced into this supercell at 4 different adsorption sites shown in fig.5.1.

For the molecule calculations the K–S wavefunctions were determined at
Figure 5.1: Top and bridge sites of ethylene on Cu(100). The blue Cu atoms are in the top layer and the red Cu atoms are in the second layer. The lower two diagrams show the diagonal orientations for the top and hollow sites.
one k–point, the Γ point of the supercell. For the calculations to determine the bulk lattice parameter, a k–point grid of \(10 \times 10 \times 10\) with 110 special points determined according to the scheme of Monkhorst-Pack [66] was required (the total energy of the system increased by 0.012 eV on going from a \(9 \times 9 \times 9\) grid to a \(10 \times 10 \times 10\) grid and by 0.003 eV on going from a \(10 \times 10 \times 10\) to a \(11 \times 11 \times 11\) grid). For the slab calculations on the \(1 \times 1\) unit cell 5 layer and seven layer slabs, a k–point grid of \(9 \times 9 \times 9\) with 15 special points was required (the total energy of the system decreased by 0.055 eV on going from a \(8 \times 8 \times 8\) grid to a \(9 \times 9 \times 9\) grid decreased by 0.0023 eV on going from the \(9 \times 9 \times 9\) to a \(10 \times 10 \times 10\) grid). On going to the \(2 \times 2\) unit cell 5 layer slab a k–point grid of \(7 \times 7 \times 7\) with 10 special points was required (the total energy decreased by 0.031 eV on going from a \(6 \times 6 \times 6\) grid to a \(7 \times 7 \times 7\) grid and by 0.009 eV on going from a \(7 \times 7 \times 7\) to a \(8 \times 8 \times 8\) grid), this being the k–point grid also used for the adsorption calculations. The initial geometries of ethylene were taken from previous calculations as detailed in chapter 4. The initial lattice parameter of copper was taken as the calculated value given above.

The electronic structure of the systems was interpreted using electron density plots corresponding to different K–S orbitals. A Mulliken population analysis was used to assess the degree of charge transfer between ethylene and copper in \(\text{Cu(C}_2\text{H}_4\) and a DOS plot was used to determine the extent of binding of \(\text{C}_2\text{H}_4\) to the copper surface.
5.3 The Adsorption of Ethylene on a Copper Surface

5.3.1 Cu(C₂H₄)

Previous studies have determined that the stable Cu(C₂H₄) complex exists but it is not immediately obvious how the species should bind. As the copper atom has a filled d shell it is not obvious whether the interaction between species should involve the d orbitals. An alternative configuration suggests the involvement of the copper 4p orbitals [115] in a stable excited state. The involvement of the copper 4p orbitals is plausible as if the d orbitals form a closed shell, the charge may be polarised on the atom which allows the closer approach of and consequently the formation of a stronger bond formed with the ligand. The scheme of Dewar [112], Chatt and Duncanson [113] has been successfully applied in the description of the charge transfer between C–C π bonds and transition metals. This scheme states that electron density is donated into empty metallic d orbitals from the π orbital with back donation from the metal into the π* orbital of the ligand. In describing the bonding within complexes where the metal is in a low oxidation state, the molecular orbital theory provides the most appropriate approach for describing the likely formation of covalent bonds in the complex.

Previous calculations on the ethylene–copper complex by Nicolas et al [115] and on the ethylene–copper dimer complex by Roszak et al [116] determine that
A stable complex exists with the copper atom placed symmetrically above the centre of the C–C bond. Both studies use Hartree–Fock based methods with basis sets derived from Gaussian type orbitals (GTOs) and the binding energies and geometries are compared with the results from this study in table 5.1.

The geometry of the complex determined here is shown in fig.5.2 and as can be seen also has the copper atom lying above the centre of the ethylene C–C bond. The binding energy of 0.786 eV was determined by subtracting the total energies of an isolated copper atom and ethylene molecule from the total energy of the complex \( E_{ads} = E_{tot} - E_{Cu} - E_{C_2H_4} \). This value for the binding energy corresponds to the amount of energy required to form a chemical bond between the two species. As can be seen in table 5.1 this value lies between the two binding energies determined by Nicolas et al [115], their lower value.
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<th>Study</th>
<th>Bind. Energy /eV</th>
<th>C–C /Å</th>
<th>C–H bend</th>
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<td>1.88</td>
</tr>
</tbody>
</table>

Table 5.1: Table comparing binding energies and bond lengths for the Cu(C₂H₄) complex. The C–H bend refers to the angle at which the C–H bond bends out of the molecular plane of ethylene and the height of Cu refers to the perpendicular distance between the centre of the C–C bond and the Cu atom.

Table 5.1: Table comparing binding energies and bond lengths for the Cu(C₂H₄) complex. The C–H bend refers to the angle at which the C–H bond bends out of the molecular plane of ethylene and the height of Cu refers to the perpendicular distance between the centre of the C–C bond and the Cu atom.

corresponding to the ground state configuration with Cu 3d¹⁰4s¹, and the higher value corresponds to the stable excited state with Cu 3d¹⁰4p¹. The weak binding in this Cu 3d¹⁰4s¹ configuration is attributed to repulsion between the electrons in the copper 4s and ethylene molecular orbitals, which can be better avoided by occupation of the copper 4p orbitals.

In the results from this study the elongation of the C–C bond by 0.056Å from its initial geometry and the bending of the C–H bonds out of the ethylene molecular plane by 4.3° indicate a weakening of the ethylene C–C π bond. The perpendicular distance of 2.023Å between the copper atom and ethylene indicate that this C–C π bond is involved in chemical bond formation with copper.

The first thing to note in the energy level diagram in fig.5.3 showing the eigenenergies of the K–S orbitals is that all the levels are split due to the presence of an unpaired electron. This causes a net spin on the molecule and therefore the electrons of different spins are no longer degenerate. In this energy level diagram a group of orbitals of low energy could be ethylene molecular orbitals
Figure 5.3: The energy level diagram for Cu(C$_2$H$_4$). The thick lines indicate two levels close together in energy. The energy level diagram on the right provides a comparison with C$_2$H$_4$. 
which are non-bonding in Cu(C_2H_4). The group of 10 closely spaced orbitals above this in energy could correspond to non-bonding d atomic orbitals on the copper atom. However, an investigation of the charge density surfaces corresponding to these K–S orbitals indicates that all the valence atomic orbitals on the copper atom and the ethylene molecular orbitals combine to form new bonding and anti-bonding molecular orbitals in Cu(C_2H_4). An example of this may be seen in figs.5.4 and 5.5 which show bonding and anti-bonding combinations of the ethylene π_y molecular orbital and a copper d atomic orbital. The highest occupied Cu(C_2H_4) molecular orbital involves a bonding combination between the ethylene π^* orbital and possibly the 4s orbital of copper, a plot of the charge density surface associated with this orbital is shown in fig.5.6. As electron density is distributed into the ethylene π^* orbital the electronic repulsion between the species was reduced. There is no evidence for the involvement of Cu4p orbitals in any of the Cu(C_2H_4) molecular orbitals.

5.3.2 The Chemical Bonding between C_2H_4 and Cu in Cu(C_2H_4)

There are several previously proposed chemical bonding schemes for Cu(C_2H_4). The possibilities are a charge transfer complex in which the unpaired electron on Cu is donated to C_2H_4, or a σ bound complex where a bond is formed between Cu and one of the C atoms, but the most likely is a Dewar [112], Chatt, Duncanson [113] interaction. For the copper/ethylene complex this would
involve two dative interactions, one in which there is donation of electron density from the \( \text{C}_2\text{H}_4 \pi \) orbitals into the Cu 4s orbital and the other in which there is back donation from a Cu3d orbital into the \( \text{C}_2\text{H}_4\pi^* \) orbital. However, a Hartree–Fock study by Nicolas \cite{115} concluded that no significant charge transfer could occur between the species as the geometry of the ethylene molecule was not perturbed in the complex. This suggested that the C–C \( \pi \) bond was not involved in any interaction. Instead they proposed a weak charge transfer interaction with the unpaired electron located mainly in the Cu4s orbital and partially in the Cu4p orbital away from the ligand.

The conclusions from this study do not agree with either of these schemes but do agree with the proposal made by Itoh \textit{et al} \cite{124} in a Hartree–Fock study where all the Cu 4d and 4s orbitals were involved in bond formation. However, in this study by Itoh the electron configuration interaction and geometry relaxation were not taken into account so nothing was concluded beyond there being an electron density transfer from Cu to \( \text{C}_2\text{H}_4 \).

The results presented here in which the ethylene molecule is significantly distorted and the binding energy of 0.786eV support the involvement of bonding and anti-bonding combinations involving all the orbitals. This combination would allow for a stronger interaction between the species than that involving only the highest and lowest occupied molecular orbitals (HOMO and LUMO) of ethylene with the copper 4s orbital. The use of a basis set based on atomic orbitals as used by Nicolas \textit{et al} \cite{115} may be more restrictive in allowing orbitals
to combine as they allow only the higher energy molecular and atomic orbitals to combine, a problem not encountered when using a planewave basis set. This would explain the differences in binding energies between the results of this study and that of Nicolas et al [115] (table 5.1).

A Mulliken analysis of Cu(C$_2$H$_4$) gave a charge of 0.18e on Cu indicating a transfer of electron density from copper to ethylene. This value indicates that the back donation from copper to ethylene is prevalent and this may be expected when it is considered that the $\pi^*$ orbital of ethylene is involved but there is no indication that the $p$ orbitals of copper are involved. The occupation of the copper $s$ orbital is increased to 1.1 electrons on complexation which indicates that this is the orbital which receives electron density from ethylene. The population of the copper $d$ orbitals was determined to be 9.7 electrons indicating that the copper $d$ orbitals are involved in bonding with ethylene, the $p$ orbitals were unoccupied. This population analysis is therefore consistent with the bonding interactions predicted from an examination of the equilibrium geometry and K–S orbital analysis.
Figure 5.4: The charge density surface associated with a K–S molecular orbital where a binding interaction occurs between the $\pi_y$ molecular orbital of ethylene and a $d_{xy}$ orbital of copper.

5.3.3 Cu(100)

Previous LEED (low energy electron diffraction) studies of the (100) [125] and (110) [125, 126] surfaces of copper show there to be an oscillatory relaxation of the atomic layers. This is when the perpendicular distance between the outer most layers relaxes from its bulk value with the spacing between the first and second layers greater than that between the second and third. The spacing between the upper most layers contracts to increase the co-ordination of the
surface atoms, and the distance between the second and third layers expands to compensate for the steric and electronic repulsion caused by the proximity of atoms in the outer layers. No reconstruction or relaxation of atoms within the surface plane was observed in these previous experiments. This oscillatory relaxation has been observed in this study in calculations done on a slab of nine layers with one unit cell in the surface plane which result in a contraction of 3.3% between the outer two layers and a 0.5% expansion between the second and third layers compared to the bulk inter-layer spacing. The distance between
Figure 5.6: The charge density surface of the Cu(C_2H_4) highest occupied K–S orbital which involves the ethylene π* orbital.

the inner layers (1.81Å) was found to be close to the bulk spacing (1.82Å). No relaxation of the atoms was detected within the surface plane.

For the adsorption calculations a slab with two by two unit cells in the surface plane was necessary to accommodate the adsorbate molecule within the cell. Although the total energy had converged with respect to the distance between the inner and outer layers of the slab on using a 7 layer slab (56 atoms), an adsorption study on such a thick slab was unfeasible. A 5 layer slab (40 atoms) was then characterised as this was considered to be the most appropriate for retaining the accuracy of the adsorption calculations while still being computationally feasible.

On relaxing the atomic positions of a 5 layer slab with 2×2 unit cells in the
surface plane, it was found that there was a surface contraction of 3.0% between
the top two layers and no relaxation within the planes parallel to the surface.
The distance between the central layers in the slab was 1.84Å, which compares
favourably with a bulk spacing of 1.82Å and a spacing of 1.81Å between the
central layers in a 7 layer slab.

5.3.4 Ethylene on Cu(100)

The adsorption of ethylene has previously been examined on Cu(111) [40, 16,
127], Cu(110) [41, 17, 42], and Cu(100) [128, 129]. These studies employed a
variety of methods to examine the system including LEED (low energy electron
diffraction), HREELS (high resolution electron energy loss spectroscopy), TPD
(temperature programmed desorption), RAIRS (resolved angle infra red spec-
troscopy) [16, 17], STM (scanning tunnelling microscopy) [41], NEXAFS (near
edge x-ray spectroscopy) [40, 128, 129], SEXAFS [42] and DFT cluster studies
[127]. All these studies conclude that ethylene does not dissociate and lies flat
with its molecular plane parallel to the surface. Also ethylene is physisorbed or
weakly chemisorbed on all the above mentioned surfaces of copper.

The four different adsorption sites shown in fig.5.1 were investigated in this
study. All were stable with the top site system shown in fig.5.1A being the
lowest in energy and therefore the favoured adsorption site. The adsorption
geometries and binding energies are shown in table 5.2. There is little difference
between the configurations of the two top site systems (fig.5.1A and C): the
CHAPTER 5. ETHYLENE AND COPPER

<table>
<thead>
<tr>
<th>Study</th>
<th>Binding Energy /eV</th>
<th>C–C /Å</th>
<th>Bend of C–H</th>
<th>Height of Cu /Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₂H₄</td>
<td></td>
<td>1.312</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₂H₆</td>
<td></td>
<td>1.513</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu(C₂H₄)</td>
<td>0.786</td>
<td>1.37</td>
<td>4.3°</td>
<td>2.02</td>
</tr>
<tr>
<td>Top site 5.1A</td>
<td>0.24</td>
<td>1.37</td>
<td>5.7°</td>
<td>2.25</td>
</tr>
<tr>
<td>Top site 5.1C</td>
<td>0.23</td>
<td>1.38</td>
<td>5.5°</td>
<td>2.25</td>
</tr>
<tr>
<td>Hollow site 5.1B</td>
<td>0.00</td>
<td>1.34</td>
<td></td>
<td>2.94</td>
</tr>
<tr>
<td>Hollow site 5.1D</td>
<td>0.00</td>
<td>1.34</td>
<td></td>
<td>2.94</td>
</tr>
</tbody>
</table>

Table 5.2: Table comparing the results of the adsorption calculations with Cu(C₂H₄), C₂H₄ and C₂H₆. The numbers associated with the adsorption systems refer to figure 5.1. The above results indicate that a weak chemisorption occurs at the top sites but physisorption occurs at the hollow sites.

ethylene molecule in both systems has a C–C bond length elongated by 0.06Å compared to its gas phase value and the C–H bonds are bent out of the plane of the molecule, away from the surface. This indicates that a chemical bond has been formed with the surface, but as the ethylene molecule is 2.25 Å above the surface, only a weak chemisorption interaction takes place. These two systems may be compared to Cu(C₂H₄) where the C–C bond length, bend of the C–H bonds out of the plane of the molecule, and perpendicular distance between copper and ethylene are similar. The binding energy of these sites is lower by 0.59eV than the binding energy of Cu(C₂H₄) and at approximately 0.2eV corresponds to a weak chemisorption interaction. The density of states plot of the adsorption system shown in fig.5.7 shows a band just below the Fermi level in which no sharp peaks, which would indicate non–bonding ethylene orbitals, can be discerned. This suggests that a chemisorption interaction occurs in which the ethylene molecular orbitals combine with the copper d band.

For the bridge site systems (fig.5.1B and D), the C–C bond lengthening by
0.03Å on adsorption is less than that observed at the top sites, and the bending the C–H bond insignificant. This, along with the greater height of ethylene above the surface which is almost 3.0Å and the binding energies which are effectively zero, suggest a weaker physisorption interaction.

Figures 5.8 and 5.9 indicate the extent of distortion of the ethylene molecule and in fig.5.9 and it is apparent that the copper atom directly below the centre of the C–C bond is raised above the surface by approximately 0.2Å in both top site systems. This is the only distortion of the surface in the adsorption systems and suggests that it is this atom in particular which forms a bond with the ethylene molecule. This indicates that there are localised orbitals on this Cu atom available for bonding with ethylene in a similar fashion to Cu(C₂H₄). However, in the surface the neighbouring Cu atoms modify the interaction by preventing a close approach for ethylene. Once the Cu atom is raised the perpendicular distance between this atom and the C–C bond is 2.05Å which is only 0.03Å greater than that in Cu(C₂H₄). The C–C bond length of the adsorbed molecule is marginally longer than that in Cu(C₂H₄) which indicates a stronger bonding interaction. This is because of the possibility of a greater electron density transfer from ethylene to the surface as the additional electron density may be delocalised more easily in the surface.
5.4 Conclusion

Studies of ethylene on transition metals such as Pt(111) [89] and Rh(111) [44] show that ethylene is adsorbed irreversibly and decomposes to give dehydrogenated fragments on the surface. The partially filled $d$ levels of these metals lead to a more reactive surface than copper, which has a filled $d$ band. The weak adsorption of ethylene flat on the surface at a top site agrees with previous studies of ethylene adsorbed on different surfaces of copper which has a filled $d$ band and subsequently is less reactive than other transition metal surfaces. The molecule does not dissociate in any of these studies and no reconstructions of the surfaces occur. This suggests that the adsorption characteristics of ethylene are similar on the (111), (110) and (100) surfaces of copper.

The results of this planewave DFT study indicate that ethylene is preferentially chemisorbed at a top site on Cu(100), with an insignificant difference between the two orientations examined. The structure of the molecule chemisorbed on the surface is similar to that of the Cu(C$_2$H$_4$) complex. This indicates that some of the ethylene molecular orbitals combine with the $d$ orbitals localised on the atom directly below the centre of the C–C bond to form a set of bonding and anti–bonding orbitals joining the molecule and the surface. Only physisorption can occur at the hollow site as there is no opportunity for the ethylene molecular orbitals to combine with $d$ orbitals localised on a surface atom.
Figure 5.7: The density of states plot for ethylene on Cu(100). No peaks which correspond to the non–bonding orbitals of ethylene may be discerned.
Figure 5.8: The structure of the adsorption of ethylene at a hollow site on the Cu(100) surface.
Figure 5.9: The structure of the adsorption of ethylene at the top site of Cu(100). 5.9A was the equilibrium adsorption site at which chemisorption occurred. 5.9C was close in energy (table 5.2) which indicates that the molecule can rotate freely about the axis which joins the surface copper atom directly below the ethylene molecule with the centre of the C–C bond.
Chapter 6

Benzene and Copper

6.1 Introduction

The adsorption of benzene on a copper surface provides an example of how a conjugated $\pi$ system of electrons on the benzene ring interacts with the $d$ band of a transition metal. The benzene molecule is shown in fig.6.1 and its structure and properties are defined by its conjugated electron structure. The $sp$ hybridised orbitals on each carbon atom combine to form a delocalised $\pi$ ring above and below the molecule. This conjugation stabilises the molecule and ensures a symmetrical structure. The characteristics of the copper surface have been described in the previous chapter.

The standard experimental technique for examining adsorption geometries is low energy electron diffraction (LEED) which relies on an ordered adsorbate layer in order to be able to interpret the diffraction pattern. When benzene
adsorbs onto a transition metal surface, the adsorbate layer is usually disordered so carbon monoxide is introduced as a co-adsorbate to induce ordering of the adsorbate molecules to enable the system to be examined. However, the presence of carbon monoxide can affect the electronic structure of the surface and therefore the interaction of benzene with the surface molecules, as well as modifying lateral interactions between benzene rings. The adsorption of isolated benzene has therefore not been studied extensively and the nature of adsorption and the adsorption geometry are disputed. A planewave DFT study allows the examination of an isolated benzene molecule adsorbs on a transition metal surface.

Experimental studies conclude that benzene lies flat, with its molecular plane parallel to the surface when adsorbed on transition metal surfaces such as Pd(111) [90], Pd(110) [130], Rh(111) [51, 54], Ru(001) [131], Pt(100) [132], Ni(110) [53], and Ni(111) [48, 49]. The same behaviour is observed when benzene is adsorbed on copper surfaces (110) [42, 43, 50, 133] and (100) [134]. At high coverages the benzene molecule stands upright, with its molecular plane perpendicular to the surface, but in most processes of interest the coverage is such that the molecule lies flat on the surface. On growing crystalline benzene the first layer of adsorbed molecules lie flat on the surface, then subsequent layers adopt the bulk structure where molecules lie perpendicular to one another in parallel layers [135]. These results would suggest that the delocalised π electron structure in benzene is crucial in determining how it binds to a metallic surface.
Although most studies conclude that benzene is chemisorbed to transition metal surfaces, the nature of binding and the precise geometry of adsorbed benzene is still under discussion. A number of possible distortions of the benzene geometry have been suggested such as bending of the C–H bond out of the plane of the molecule, forming a crown distortion [136]; expansion of the benzene ring [136]; Kekule distortion [51], where the C–C bond lengths within the ring alternate between that typical for single and double bonds; and a boat like distortion [43] where the planarity of the ring is broken which allows some carbon atoms to lie closer to the surface than others. The nature and extent of these distortions is dependent on the way in which the benzene molecule is aligned with and binds to the surface. Usually the molecule orientates itself to ensure maximum overlap of the carbon p orbitals with the metal atom d orbitals. According to the scheme of Dewar, Chatt and Duncanson [112, 113] there is transfer of electron density from the benzene π orbital into vacant metal d orbitals and back donation from the metal d orbitals into the benzene π* orbital. The loss of electron density from the π orbital and occupation of the π* orbital in benzene leads to a loss of the electron conjugation. The extent of this loss of conjugation is dependent on the amount of charge transfer and therefore the extent of orbital overlap.

Benzene typically adsorbs at a site which ensures the maximum possible overlap of its orbitals with the d orbitals on the metal atoms. The equilibrium adsorption configuration is dependent mainly on competition between increasing the overlap of the orbitals and retaining the stable structure of the benzene.
Experiments report only minor distortions of the benzene ring with the extent of distortion dependent on the occupancy of the $d$ band after adsorption has taken place. The nature of the adsorption and the extent of distortion of the benzene ring are therefore of interest in a study of benzene on Cu(100). As copper is a noble metal with an almost full $d$ band, the adsorption interaction is likely to be weaker than that on other transition metal surfaces. In order to characterise the adsorption interaction a similar approach is taken to that outlined in chapters 4 and 5. Initially the binding within a Cu(C$_6$H$_6$) cluster is determined and then adsorption of benzene onto a slab of Cu(100) is examined. From using the results from the Cu(C$_6$H$_6$) calculations, the adsorption behaviour of benzene can be explained.

After a brief outline of the input parameters for the calculation, the results and a discussion about the Cu(C$_6$H$_6$) and adsorption calculations is given in the last section.

### 6.2 Details of the Calculations

The VASP code was used for all calculations presented in this chapter. The spin dependent general gradient approximation [65], with the Vanderbilt ultrasoft pseudopotentials [68, 69] were implemented. As the elements in this system are the same as those examined in chapter 5, the same planewave cutoff energy of 350eV is used.
CHAPTER 6. BENZENE AND COPPER

The Cu(C6H6) calculations required a supercell size of and calculations of an isolated benzene molecule required a supercell of dimensions of 13×13×13. One k-point was used at the Γ point of the cell for both these systems. The adsorption calculations were done on a 5 layer slab which had 2×2 unit cells in the surface plane and is the same as that used for the ethylene adsorption calculations in the previous chapter. In these adsorption calculations only the geometry of the benzene molecule was allowed to relax and the slab was kept fixed in order to make the calculations computationally feasible. Although a slab with 3×3 unit cells in neighbouring cells would have ensured a separation of 5 Å between benzene molecules in the surface plane, the total energy of this cell did not converge on relaxation of the atomic positions. No significant influence of neighbouring benzene molecules on the adsorption system such as repulsions or attractions between the adsorbate molecules was observed in the calculations. It was ensured that there was a vertical distance of at least 5 Å between species in adjacent supercells. This calculation required a k-point density of 7×7×1 giving 10 special points, the convergence of the total energy being checked with respect of the number of k-points.

6.3 Cu(C6H6)

The binding between benzene and transition metals has been of interest as a model system for investigating the π–d interaction. Although this interaction
is common in many complexes, its nature has remained elusive until the advent of gas phase spectroscopy and computer simulation. This interaction can only be examined in complexes in condensed phases in which individual bonds are difficult to examine. Benzene is capable of forming a variety of complexes with different transition metals. It favours a sandwich type structure, with metal atoms placed between (sandwiched) by benzene rings for early transition metals, and a ball like structure with a number of benzene rings surrounding a number of metal atoms in the centre of the ball for later transition metals [137]. However, for copper only the Cu(C\textsubscript{6}H\textsubscript{6}) and Cu\textsubscript{2}(C\textsubscript{6}H\textsubscript{6}) complexes may be formed according to a mass spectrometry study by Kurikawa et al [137]. The binding within the more stable [Cu(C\textsubscript{6}H\textsubscript{6})\textsuperscript{+}] complex has been studied more extensively using computer simulation [138, 139]. These studies determine a symmetrically bound complex with the copper ion above the centre of the benzene ring. However, in the other noble metal complexes Au\textsuperscript{+}(C\textsubscript{6}H\textsubscript{6}) and Ag\textsuperscript{+}(C\textsubscript{6}H\textsubscript{6}), there is a small energy difference between complexes where the metal atom adopts different positions above the ring [138]. There is less information on the Cu(C\textsubscript{6}H\textsubscript{6}) complex apart from it being weakly bound with a comparatively low ionization energy.

In this study three different configurations of Cu(C\textsubscript{6}H\textsubscript{6}) were examined (fig.6.1): one with the copper atom placed symmetrically above the centre of the benzene ring, one with the copper atom above a carbon atom, and one with the copper atom above the centre of a C–C bond. The total energy was converged when
Table 6.1: The binding energies and heights of the copper atom above the benzene ring for the three configurations of Cu(C₆H₆) examined.

<table>
<thead>
<tr>
<th>Position</th>
<th>Binding Energy /eV</th>
<th>Height /Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Centre</td>
<td>0.403</td>
<td>2.191</td>
</tr>
<tr>
<td>Over C</td>
<td>0.617</td>
<td>2.097</td>
</tr>
<tr>
<td>Over bond</td>
<td>0.314</td>
<td>2.731</td>
</tr>
</tbody>
</table>

The geometry of each one was relaxed. Their binding energies and geometries are compared in table 6.1 and fig.6.2. The binding energies are determined by subtracting the total energy of the isolated copper atom and benzene molecule from the total energy of the complex \( E_{\text{bind}} = E_{\text{tot}} - E_{\text{atom}} - E_{\text{mol}} \) and range from 0.314eV to 0.613eV. These values for the binding energy are consistent with chemical bond formation between the species. The heights of the copper atom above the benzene ring range from 2.097Å to 2.731Å are again consistent with a chemical bonding interaction. The configuration with the copper atom placed directly over a carbon atom is the most stable. This would suggest that an adsorption site on a copper surface would be favoured which allowed the maximum alignment between copper and carbon atoms.

As shown in fig.6.2, there are no major distortions of the benzene ring on complexation. The C–C bond length in the configuration with the copper atom above the centre of the benzene ring of 1.400Å is identical to that in the calculated isolated benzene molecule. There is also no detectable bending of the C–H bonds out of the plane of the molecule so bonding to the copper atom does not noticeably perturb the benzene geometry. In the configuration where the copper atom is placed above a carbon atom, the benzene ring was perturbed slightly as
Figure 6.1: Diagram giving a view from above of the three positions of the copper atom placed above the benzene ring. The position of the copper atom is marked by a shaded circle.

The carbon atom below the copper atom bent out of the plane of the molecule by 3.4° towards the copper atom (fig.6.2). The C–H bond associated with this carbon atom then bent away from the copper atom. For the configuration with the copper atom above the centre of a C–C bond, this bond was raised above the plane of the molecule (fig.6.2) towards the copper atom. In each configuration the benzene geometry is not greatly perturbed suggesting that the molecule lies parallel to the surface on adsorption.

The energy level diagram shown in fig.6.3 also suggests that the configuration with the copper atom positioned above a carbon atom is the most stable. There are a greater number of occupied K–S orbitals at a lower energy which results in a
comparatively lower total energy of the molecule. The least stable configuration with the copper atom above the centre of a C–C bond has comparatively higher energy occupied K–S orbitals.

The charge density surfaces corresponding to the K–S orbitals show that the molecular orbitals of benzene and the $d$ atomic orbitals of copper combine in a series of bonding and anti-bonding combinations (fig.6.4). The lowest occupied
Figure 6.3: The eigenenergy level diagram of the occupied K–S orbitals of Cu(C₆H₆). Part A corresponds to the configuration with the copper atom placed over the centre of the benzene ring, part B corresponds to the copper atom over a carbon atom, and part C corresponds to the copper atom over the centre of a C–C bond. The energy scale is in eV.

K–S orbitals of Cu(C₆H₆) are non–bonding benzene orbitals (fig.6.5), for higher energy benzene orbitals it is possible to form combinations with the \( d \) orbitals of correct symmetry. The highest occupied molecular orbital (HOMO) could be a binding combination between the benzene \( \pi \) orbitals and a \( s–p \) hybrid orbital on the copper atom. Fig.6.6 shows a K–S orbital similar to that shown in fig.6.4, but this time the copper atom is above a carbon atom in the benzene ring. As can be seen, similar combinations can be formed between the species for all three configurations, the most stable are those which allow the greatest overlap of the orbitals.
6.4 Adsorption of Benzene on Cu(100)

The adsorption of benzene on Cu(100) was investigated by examining four different adsorption sites (fig.6.7). The sites are defined by the alignment of the centre of the benzene ring with the surface atoms. The top site, with the centre of the benzene ring directly above a surface copper atom, and the hollow site, with the centre of the benzene ring directly above a hollow spacing, were found to be at local minima on the adsorption potential surface. These states remained as local minima when the rings were rotated by 30° about the adsorption site as shown in fig.6.9. The other two sites as shown in fig.6.8 were not local minima.
Figure 6.5: Charge density surface corresponding to the lowest energy non-bonding K–S orbital of benzene in Cu(C₆H₆).

<table>
<thead>
<tr>
<th>Adsorption Site</th>
<th>Binding Energy /eV</th>
<th>Height /Å</th>
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<tbody>
<tr>
<td>Hollow</td>
<td>0.031</td>
<td>2.45</td>
</tr>
<tr>
<td>Hollow Twisted</td>
<td>0.033</td>
<td>2.49</td>
</tr>
<tr>
<td>Top</td>
<td>0.000</td>
<td>3.11</td>
</tr>
<tr>
<td>Top Twisted</td>
<td>0.000</td>
<td>3.04</td>
</tr>
</tbody>
</table>

Table 6.2: The binding energies and height of benzene above the surface for two orientations of the benzene ring examined at the hollow and top sites shown in fig.6.9.

and the benzene ring relaxed away from the surface and from the sites before convergence of the total energy was achieved.

The results presented in table 6.2 show there to be weak chemisorption at the hollow site with a binding energy of 0.03eV and a height of about 2.5Å of benzene above the surface, and physisorption of benzene at the top site with a height of about 3.1Å of benzene above the surface. For both sites there is little difference in the adsorption characteristics between the two orientations.
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Figure 6.6: The charge density surface of a K–S orbital of the same interaction depicted in fig.6.4 except here the copper atom is positioned directly over one of the carbon atoms of the benzene molecule. The figure on the left hand side is a side view of that shown on the right hand side.

of the molecule at the sites examined. The chemisorption energies are lower than what would be expected considering the distances between the adsorbate and substrate. This may be explained by considering that energy is required to distort the benzene molecule on adsorption but this is compensated by the energy gained from bond formation between the carbon and copper atoms. This results in a low net binding energy but with the adsorbate close to the surface.

There was a boat distortion of the chemisorbed benzene molecule at the hollow site (figs.6.9 and 6.10). The bonding occurred between two para carbon atoms in the benzene ring and two copper surface atoms. Two C–C bonds were shortened to align the carbon atoms with the surface copper atoms as shown in fig.6.10 and the hydrogen atoms attached to these bonding carbon atoms are bent away from the surface at an angle of 6.3° out of the plane of the molecule.
Figure 6.7: The four adsorption sites investigated in this study. The location of the points corresponds to the alignment of the centre of the benzene ring. The (untwisted) orientation of the benzene molecule is shown to the left of the slab. The hollow and top sites are at local minima. Sites 3 and 4 did not correspond to minima in the adsorption potential surface and are shown in fig.6.8.

The hollow site allows the closest alignment of two of the carbon atoms with two of the surface atoms as shown in fig.6.9. The interaction is not as strong when the benzene ring is in its twisted orientation, where the alignment of the carbon atoms with the underlying copper atoms is not as close. The geometry of the benzene ring is distorted in order to allow the carbon and copper atoms to be closer, with the two carbon atoms 0.03 Å closer to the surface than the other four carbon atoms in the ring. This allows the optimisation of the strongest interaction predicted by the complex molecule calculations, with a copper atom...
directly above a carbon atom. This deformation was observed on the Cu(110) surface of copper in a DFT cluster model study by Pettersson et al [43]. This compared the benzene structure with that of the triplet excited state of a benzene molecule in the gas phase and suggested that there would be an energy barrier to formation of this adsorbed phase. This observation would correspond to what has been determined here.

The charge density surface (fig.6.10) and density of states (fig.6.11) plots indicate that chemical bonding occurs at the hollow site. There is an accumulation of charge density between the species as shown in fig.6.11 and no peaks which indicate non-bonding benzene orbitals can be discerned in fig.6.12. Together with the information obtained from the complex molecule calculations, this indicates that the $d$ orbitals localised on the surface copper atoms participate in forming new bonding and anti-bonding orbitals with the benzene atom in a similar fashion to the bonding within a complex molecule.

There was no significant distortion of the benzene molecule, compared with the molecule in the isolated gas phase, at the top site. There is a chemical bonding interaction in the corresponding complex molecule but the top site alignment which makes this interaction favourable is counteracted by the energy required to distort the benzene ring being greater than that gained by bond
formation. There is no alignment of the carbon atoms or the centre of the benzene ring with the surface copper atoms at the sites shown in fig.6.8 which results in no adsorption interaction at these sites.

No relaxation of the copper surface on adsorption of a benzene molecule has previously been reported which supports the conclusions drawn from this study where the surface atoms were not permitted to relax. Cu(100) has been shown to be stable and unreactive. In the ethylene/Cu(100) adsorption system discussed in the previous chapter only the copper atom directly involved in the bond to the adsorbate moved up from the surface. This suggests that the same is possible for the benzene/Cu(100) system where the copper atoms directly below carbon atoms could move out of the surface plane. This would not change the structure of the adsorbate significantly though.

6.5 Conclusion

This study has determined that benzene is chemisorbed at a hollow site on Cu(100) and physisorbed at the top site. The binding is shown to be dependent on the alignment of the carbon and surface copper atoms which results in the combination of $d$ orbitals localised on the surface copper atoms with the benzene molecular $\pi$ orbitals. Previous studies have shown benzene to be chemisorbed on copper surfaces [42, 43, 140] with a low barrier to diffusion across the surface. Benzene is more strongly adsorbed on other transition metals. For instance
the distance between benzene and the Ni(111) surface is 1.92Å [48], and with Ru(100) is 2.12 Å [131] compared to 2.45Å determined for Cu(100) here. A cluster model study by Anderson et al [141] found the extent of distortion of the benzene ring, and therefore the strength of the interaction, to be dependent on the occupancy of the $d$ band by a comparison of adsorption on Ni(111), Pt(111) and Ag(111). The binding of the benzene molecule to the Ag(111) surface was significantly weaker than that to Ni(111) and Pt(111). This indicates that charge transfer to the $d$ band from the adsorbate is important for a strong bonding interaction with the substrate. Therefore it would be expected that there would be only weak chemisorption of benzene on a copper surface as predicted in this study.

This study has characterised the adsorption of an isolated benzene molecule on a copper surface. As has already been stated this only represents the adsorption system at low coverages and temperatures. Studies of benzene adsorption on Pd(111) [90] and Rh(111) [51] have shown the adsorption configuration to be dependent on the surface coverage, the benzene molecule is tilted or adapts a Kekule structure respectively at higher coverages. This suggests that there would be a greater distortion of benzene at higher coverages. Also the molecule becomes mobile on transition metal surfaces at temperatures above 350K but does not decompose and desorbs molecularly. The results from this study demonstrate how it is possible for a molecule with a delocalised $\pi$ system to bind to a noble metal surface. However, the binding characteristics are likely to be
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sensitive to the environment and physical conditions of the adsorption system.
Figure 6.8: The two sites which did not correspond to local minima in the adsorption potential surface.
Figure 6.9: The two sites which did not correspond to local minima in the adsorption potential surface.
Figure 6.10: A top view (A) and a side view (B) of the geometry obtained at the hollow site. The green atoms correspond to top layer copper atoms and the blue toms to second layer copper atoms. (The top site may be visualised by switching this assignment of colours.)
Figure 6.11: The charge density surface of benzene adsorbed at a hollow site. There is clearly a build up of charge density between the two species which indicates a chemisorption interaction.
Figure 6.12: The density of states plot for benzene adsorbed at a hollow site on Cu(100). No peaks which correspond to non-bonding benzene orbitals can be discerned.
Chapter 7

Conclusion

The study of the adsorption of ethylene and benzene on low index aluminium and copper surfaces provides a model for the adsorption of π bonded molecules on s–p and noble metal surfaces. This study has determined that ethylene and benzene are chemisorbed on the (100) of copper, but physisorbed on the (100) face of aluminium. For the chemisorption interactions on the copper surface it was found that the alignment of molecular orbitals with d orbitals localised on copper surface atoms was important for the determination of the adsorption site, orientation of the molecule on the surface, and strength of the interaction. A chemisorption interaction between ethylene and aluminium could not occur because of the diffuse nature of the metal s–p band which did not overlap with the ethylene molecular orbitals. It is known that ethylene and benzene are adsorbed molecularly on the noble metal surfaces, but dissociation can occur on other transition metals surfaces where there is greater charge transfer between
the species as a result of the partially occupied \( d \) band.

The chemisorption interaction has been found to be a local interaction on the surface. The structure of the system and nature of the binding interaction may be predicted from the molecule calculations. This suggests that the molecular orbital description of the adsorbate/substrate interaction is a valid and useful way of interpreting the electronic structure of the adsorption system. The binding energy is weaker for chemisorption on the extended surface than for the binding of an ethylene or benzene molecule to an isolated copper atom. This is because of a greater electrostatic repulsion between the molecule and the surface, and the delocalised electronic structure of the metal which allows the occupation of anti-bonding orbitals formed between adsorbate and substrate.

For ethylene the binding interaction occurs when the centre of the C–C bond is aligned directly above a copper atom. In the benzene adsorption interaction, a binding interaction is achieved by the alignment of the carbon atoms within the molecule above surface copper atoms. This result has implications for the determination of how liquid crystal molecules bind to a copper surface. The liquid crystal systems are more complex than the adsorption of an isolated benzene molecule, so any inferences made from this study are limited in their application. It has been shown that a substituent placed on a benzene ring can influence the adsorption behaviour of the adsorbate. A study on the adsorption of 3-thiophene carboxylate on Cu(110) by Frederick et al [142] determined that the molecule lay flat on the surface at low coverages, bonded through the benzene ring, but
at high coverages was bonded through the acid group and was perpendicular to the surface. Factors such as surface coverage, which both modifies the interaction between adsorbate and substrate and introduces an additional interaction between adsorbates, influence the adsorption structure and bonding. However, this study shows that the benzene molecule may chemisorb while lying flat on the copper surface at low coverages, and therefore it is possible that a liquid crystal molecule may adsorb via its phenyl rings.

The fact that the characteristics of the adsorption system have shown to be dependent on how the electronic structures of the species may be combined, indicates the importance of an accurate description of each one. This is facilitated by the planewave DFT calculations performed here which allow the description of the molecular and surface electronic structures within the same framework. The differences in the results for the molecule and extended surface calculations illustrate the importance of a full description of the electronic structure of the surface in the characterisation of the adsorption interaction. However, the results of the molecule calculations have been successfully used to rationalise the results of the adsorption calculations.
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