Theoretical and computational study of unusual high pressure phases in metals.

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Abstract

The work presented in this thesis is primarily concerned with the use of so called “first principles techniques” to study the behaviour of metallic elements. More specifically, we present the results of *ab initio* calculations of barium and the three heaviest group-V elements: bismuth, antimony and arsenic. Investigations started after Nelmes *et al.* showed that the elusive structure of the fourth phase of barium is very complex and consists of two parts: an octagonal “host” with chains of “guests” through the centres. The ratio of the repeating lengths of these two competing structures is irrational. Our calculations have confirmed the stability of this unusual “hotel” structure in both barium and bismuth.

Barium is also known for having two hexagonally close packed phases at lower and higher pressures than the hotel structure. Although the two hexagonally close packed phases have different properties we show that barium would transform continuously between these phases but for the intercession of the hotel phase. The differences between the two are predominantly caused by the progressive transfer of electrons from s-type orbitals to d-type orbitals.

At ambient pressures the group-V elements have a rhombohedral structure which is a distortion of a simple-cubic arrangement. As the pressure is increased the distortion decreases and the rhombohedral structure transforms continuously back to simple cubic. Experimentally however, a first order discontinuous transformation is seen in arsenic. In bismuth and antimony, transitions to completely different structures occur before the rhombohedral to simple cubic transition can occur. A Landau-type model is developed to describe the rhombohedral distortion. This model predicts a gradual transfer to simple cubic, not only with increasing pressure but also with increasing temperature. Although this prediction is confirmed with some molecular dynamics calculations there is unfortunately no experimental data.

As well as *ab initio* calculations we also present a many-body interaction potential which is based on that of Finnis and Sinclair but which describes separately s- and d-type electrons. With this potential it is possible to get a transfer of electrons from s-type orbitals to d-type orbitals as the pressure is increased. It is also able to produce an iso-structural transition with a volume collapse. By considering spin bands, the model can also be modified to model magnetic systems.
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Chapter 1

Introduction

The interest in the structure of materials has a very long history. Although by no means the first to be interested, Abbé Haüy is often considered to have started the modern scientific approach to investigations when he studied the structure of Calcite in 1815 [10]. By repeatedly splitting and measuring the angles between the phases he concluded that calcite must be made of a tiny repeating structure. He went on to study many other crystals and published his findings in a book entitled *la Loi de Symmetrie*. The resulting ideas about symmetry and Bravais lattices were developed through the 19th century. Later, Percy W. Bridgman made extensive studies of the high pressure phases of many elements. He started experimental work in 1908 after finishing his Ph.D. [1]. Working predominately by himself, he designed his own apparatus which he used to study the relation between the pressure applied and the volume of the sample, and other physical properties. By careful measurements he was able to accurately determine the pressures at which first order phase transitions occurred as well as the corresponding density of the material. Today his work provides a valuable check on any new proposed structures: if the proposed density and volume changes are significantly different, then the suggested structure is likely to be wrong. In 1946 Bridgman received the Nobel prize in recognition of his work.

In 1912, Lax von Laue proposed that X-rays may be used to identify the atomic arrangements within a crystal. Later, W. L. Bragg derived his well known equations which link the properties of the crystal structure to the positions of the maxima and minima in the diffraction pattern. In 1915 he and his father received the Nobel prize for their study of crystal structures with
CHAPTER 1. INTRODUCTION

X-rays [29].

Given the length of time over which the structures of high pressure phases have been studied, one might be forgiven for thinking that everything is known. However, with recent improvements in techniques and equipment, significant new developments have been made within the last few years. Developments such as coherent synchrotron X-ray sources and the use of diamond anvil cells [1] have lead to the increased resolution of X-ray crystallography experiments and the ability to routinely study samples at pressures up to about 50 GPa. Coupled with these improvements, techniques for growing large single crystals of the high pressure phases have enabled the identification of several previously unsolved complicated structures [64, 51, 77]. The improved techniques have also challenged the identity of previous identified phases [1].

Although obviously not as long as the history of experiments, computational studies have now been carried out for 50 years [34]. In 1954 Frank Herman used the orthogonalised plane wave method to calculate the band structure of silicon. This was very important in explaining the anisotropic masses of the electrons and the existence of light and heavy holes. The early calculations were done on what was then the state of the art paper tape computers which could hold a mere 1024 instructions. Since then both the power of computers and the theory behind the calculations have seen major advances. The field of ab initio simulations has developed greatly, particularly in the last twenty years. These developments have lead to a dramatic increase in the complexity of the systems which can be studied computationally. One thing that has not changed however, is the way in which computational physics continues to stretch the capabilities of our current computers right to their limits.

1.1 The unusual structure of Ba IV

One of the newly identified structures is that of the fourth phase of barium. The then unique structure was identified in 1998\(^1\) by Nelmes et al. [64] but was later shown to be present in a wide variety of other elements, namely arsenic, antimony and bismuth. About the same time, and independently Schwarz’s group in Germany proposed a similar structure for phase-IV in

\(^1\)although not actually published until 1999
rubidium [77]. The structure was found to consist of two interpenetrating parts which require separate descriptions. When viewed along the c-axis, the eight constituent atoms of the first structure, or host, form an octagon. However, the atoms are distributed alternately between two levels. The guest structure consists of chains of atoms which pass through the centre of these octagons. The ratio of the separations between atoms within a guest chain, to the vertical separation of the octagonal rings is irrational. Schwarz et al. however suggest that the ratio in rubidium is rational.

In barium, the high and low pressure neighbouring phases of this hotel structure both have an hexagonally close packed structure, but with different characteristics. In the low pressure hcp phase, phase II, the ratio of the lattice parameters c and a shows a strong dependence on pressure. In contrast, the same ratio in the high pressure occurrence, phase V, is almost independent of pressure.

The transition pressures in bismuth have been accurately known for some time. Their accuracy is such that bismuth is often used for calibrating pressure measurement apparatus. However, the structure of phase III has remained a mystery. It has now been shown [52] that it too assumes the hotel structure. The other two heavy elements in group V (arsenic and antimony) have also been shown to form hotels. These three elements also all have a rhombohedral structure at ambient pressure. The rhombohedral structure is a distortion from simple cubic. There is some debate over whether there is a separate simple cubic phase in these elements: Some authors report seeing a rhombohedral to simple cubic transition whereas others failed to observe such a transition.

In this thesis we present the results of ab initio calculations and theoretical studies of the elements and their various phases. The ab initio calculations make no a priori assumptions about the solutions nor about what is important or unimportant. These calculations are performed using the now well proved density functional theory. The Kohn-Sham wave functions are expanded in terms of plane waves and the ions are normally represented by ultra-soft pseudopotentials. The calculations allow us to explore the relative stabilities of different structures. They also allow individual structures to be studied at all pressures, even those pressures at which the structure is not the most stable and therefore not seen experimentally. Theoretical
and computational studies also allow the effects of other parameters which cannot be varied experimentally, to be investigated. Example parameters are the ratio of lattice vectors, cell angles and ion positions. Although the main calculations were done with large, commercially available programs, many small programs were written to analyse data. Programs were written in a variety of languages to plot band structures, calculate radial distribution functions and generally simplify data extraction. The largest and most complicated program written was that to calculate phonon dispersion curves and densities of states. The program also calculates zero-point energies and other thermodynamic properties from the densities of states.

1.2 Empirical potentials

Semi-empirical models for metallic binding have had a long and successful history in computer modelling. They are however, insufficient to describe correctly some of the behaviours of elements at high pressures. As the pressure is increased elements undergo changes in their electronic configuration. In many systems these changes drive other, more apparent structural changes which can be easily seen experimentally. Specifically, as the pressure is increased, initially unoccupied d-type bands decrease in energy and sink below the Fermi energy. This causes a transition of electrons from the valence s-type (and p-type) bands into the d-type bands. Although this behaviour may be described accurately by existing first principles calculations, the expense of such calculations dictates that a simpler model is required in order to study large scale systems. We therefore present a simple many body potential which describes separately the s- and d-type bands. In 1984 Finnis and Sinclair [22] proposed a simple model for the interactions of transition elements which comprises two parts. The repulsive part is simply the sum of the pair-wise repulsions between atoms. The cohesive part however is proportional to the width of the valence electron band. The band width of an atom is determined according to the second moment approximation [18] from the number of and proximity to its neighbours.

We have developed a model which is based on that of Finnis and Sinclair but has two bands. The interaction potential therefore incorporates 5 parts: there are separate cohesive and repulsive parts for s-type and d-type electrons and the fifth term is essentially a promotion energy
from one band to the other. As well as studying systems which are known to exhibit electron transfer from orbitals of one type to orbitals of another, this model could also be used as an alternative to the core-softened potentials [81]. These were originally proposed as potentials which may have extra phase transitions in order to describe the reported iso-structural transitions in cerium and caesium. Our model could also be used to describe magnetic materials such as iron and therefore could potentially be used in models of the earth.

1.3 Publications

Various parts of this thesis have been submitted for publication in journals; for completeness the references are given in the bibliography as well as here.


1.4 Overview of this thesis

The remainder of this thesis is laid out as follows:

Chapter 2 outlines the theory, approximations and methods used in the \textit{ab initio} calculations presented later. Chapter 3 describes how the vibrational modes may be determined. The calculation of the zero-point energies and thermal properties are also explained, as are the complete rewriting of and further developments by the author to an existing computer program.

Chapter 4 presents the results of the calculations on the rhombohedral phases of the heavy group V elements: arsenic, antimony, and bismuth. Both static and molecular dynamics calculations have been performed, and are used along with other models to discuss the possible
existence of a rhombohedral to simple cubic phase transition. Chapter 5 discusses in detail the
hotel structure and the difficulties in performing \textit{ab initio} calculations. The other phases of
barium, including the hcp phases, and the group V elements are investigated in chapter 6. The
transitions between the phases are also studied.

Chapter 7 outlines existing empirical potentials and then derives our new two-band model. The
parametrisation of the two-band model, so that it can be used to describe caesium, is also given.
Finally, the application of the model to (magnetic) iron is formulated.
The equilibrium properties of atomic systems may be obtained from quantum mechanical calculations. Properties such as the ground state electronic and geometric structure may be determined directly by calculating the total energy of the system and minimising it with respect to the electronic and ionic degrees of freedom. Once the ground state structure has been determined, many other properties such as the vibrational modes, specific heat capacities and elastic constants may be calculated by displacing the atoms slightly or by distorting the unit cell, and calculating the resulting forces on the ions and the change in internal energy.

When doing quantum mechanical calculations, as few as possible assumptions and approximations are made. If as here, the wave functions are expanded in terms of a plane wave basis set, then no a priori assumptions are made about their form. Consequently, quantum mechanical calculations are often described as being ab initio.

The field of ab initio calculations has made great advances over the last twenty years in particular and is now relatively mature. They are routinely used for studying complicated atomic systems with efficient programs for doing the calculations now commercially available. The theory behind the calculations is now well developed and thorough discussions exist elsewhere [67, 55, 76]. The subject is now also covered, partially at least, in text books such as those by Sutton [83] and Mizutani [56]. What follows in this chapter is therefore a brief overview of the theories and techniques behind the calculations.
2.1 Born-Oppenheimer Approximation

Since ions are typically between 1000 and 10000 times more massive than electrons, the electrons move around much faster than do the ions. Under the Born-Oppenheimer approximation \[83\], it is assumed that the electrons are always in their ground state, irrespective of any movement of the ions. It is therefore possible to neglect the motion of the ions in the first instance and use their positions as fixed parameters in the potential term of Schrödinger’s Equation, which defines the electron wave functions.

2.2 Schrödinger’s Equation

As the interactions between electrons and between electrons and ions is quantum mechanical in nature, it is necessary to use Schrödinger’s Equation to describe such systems. For very small systems such as the hydrogen atom, it is possible to solve Schrödinger’s equation exactly. For larger systems containing several electrons and ions, however, the problem becomes a many body problem and is therefore unsolvable. The size of the problem may be imagined by considering a centimetre cube of metal. Each electron contributes three degrees of freedom. The total number of variables is thus of order \(10^{23}\). The problem is further complicated by the fact that electrons with different spins interact differently than do electrons with the same spin. Fortunately, various approximate methods exist which allow us to solve Schrödinger’s equation and hence determine numerous properties of these systems. In 1964, Hohenberg and Kohn proved a theorem \[38\] which states that all properties of a system may be expressed as unique functionals\(^1\) of only the electron density \(n(r)\). This has the huge advantage that the electron density is a function of only three variables! However, as we will see in section 2.10, whilst this greatly simplifies the problem, it does not solve it.

In the mean time we will consider the one-electron Schrödinger equation and ignore electron-electron interactions unless otherwise stated in order to simplify the explanation of the following ideas. The full Schrödinger equation for the many-body wave function \(\Psi\) for a solid is:

\(^1\)A functional is a function of a function
2.3 Periodic Systems

Consider a perfect infinite crystal. For simplicity, suppose that all the atoms are of the same species and are regularly spaced. The following ideas may be easily generalised by considering supercells, see section 2.14.5 for more details.

Since all the atoms are equivalent, observable quantities must be invariant under translation by an integer multiple of atomic separations. That is not to say that the states of neighbouring atoms must be the same because this is not true since states are not quantum-mechanical observables. The distribution of charge $\rho$ throughout the crystal, however, should be invariant under such a translation. If $\mathbf{R}$ is a lattice vector, that is a vector which goes from one point in the lattice to another equivalent point, then the relationship

$$\rho(\mathbf{r} + \mathbf{R}) = \rho(\mathbf{r})$$

must hold. Since the charge density is given by $e \sum_j \psi_j^*(\mathbf{r}) \psi_j(\mathbf{r})$, where $e$ is the charge on an electron, the wave functions at $\mathbf{r}$ and at $\mathbf{r} + \mathbf{R}$ may differ only by a phase factor:

$$\psi_j(\mathbf{r} + \mathbf{R}) = e^{i\theta} \psi_j(\mathbf{r}).$$
According to Bloch’s theorem, the phase difference $\theta$ may be written as the product of the wave vector $\mathbf{k}$ and the lattice vector $\mathbf{R}$. Further, it is possible to write the wave function simply as the product of this phase factor with another function which has the same periodicity as the lattice. Thus,

$$\psi_j(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}} f(\mathbf{r})$$

(2.6)

where $f(\mathbf{r} + \mathbf{R}) = f(\mathbf{r})$. Although the wave vector $\mathbf{k}$ may assume any value, it is normally restricted by convention to be within the first Brillouin Zone without loss of generality. If the unit cell contains $2m$ electrons then there are $m$ doubly occupied energy bands each having a different $f(\mathbf{r})$ (labelled by $j$) at each wave vector $\mathbf{k}$. The electron states are labelled by $\mathbf{k}$ and $j$. Thus Bloch’s theorem gives the basis of band-structure theory which is very important in much of condensed matter physics. Although the Bloch wave functions are not periodic the observable quantities are.

### 2.4 Plane Waves

Unfortunately, the form of $f(\mathbf{r})$ in equation 2.6 is unknown, save for the fact that it is periodic and has the same periodicity as the lattice. Since it is periodic, we can make a Fourier series expansion in terms of plane waves of $f(\mathbf{r})$. Only those plane waves whose wave vectors are reciprocal lattice vectors, $\mathbf{G}$, have the same periodicity as $f(\mathbf{r})$ and hence have non zero coefficients in the expansion. The wave functions therefore adopt the form

$$\psi_{j,k}(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}} \sum_{\mathbf{G}} C_{j,k}(\mathbf{G}) e^{i\mathbf{G} \cdot \mathbf{r}}$$

$$= \sum_{\mathbf{G}} C_{j,k}(\mathbf{G}) e^{i(\mathbf{G} + \mathbf{k}) \cdot \mathbf{r}} .$$

(2.7)

Whilst theoretically there are an infinite number of plane waves in this representation of the wave function, in practice it is necessary to truncate the series. All plane waves whose kinetic energy, $\hbar^2 |\mathbf{k} + \mathbf{G}|^2 / 2m_e$ is below a certain value, $\epsilon_c$ are included. Normally this includes a few thousand plane waves. See section ?? for a discussion on the choice of $\epsilon_c$.

In the vicinity of the core the wave functions of valence electrons oscillate rapidly. This is because the exclusion principle requires that it must be orthogonal to the highly localised core.
2.5. ORTHOGONAL PLANE WAVES

In order to properly describe the valence wave functions in this region lots of plane waves are required, in fact so many as to make the calculations unfeasible! Luckily however, the core part of the wave function only has a small effect the chemical bonding.

2.5 Orthogonal Plane Waves

In 1940, Herring [17] suggested that the number of basis functions would be greatly reduced if functions which were orthogonal to the core states were used. He proposed the use of orthogonalised plane waves (OPW), defined by

\[ \phi_k(r) = e^{i\mathbf{k}\cdot\mathbf{r}} + \sum_c A_c\psi^c_k(r), \] (2.8)

where \( \psi^c_k \) are the normalised core-level wave functions and the sum is over all the core levels. So that these functions are indeed orthogonal to the core wave functions \( A_c \) must be

\[ A_c = -\int \psi^c_k(r) e^{i\mathbf{k}\cdot\mathbf{r}} d\mathbf{r} \] (2.9)

However, since core wave functions are localised on a particular atom they do not satisfy Bloch’s theorem and hence are unusable here. Fortunately, suitable functions may be created by simply superimposing core wave functions from all atoms:

\[ \psi^c_k(r) = \sum_R e^{i\mathbf{k}\cdot\mathbf{R}}\psi^c(\mathbf{r} - \mathbf{R}) \] (2.10)

where \( \psi^c(\mathbf{r}) \) is the corresponding wave function of the free atom. The wave functions may thus be written

\[ \psi_k(r) = \sum_G C_k(\mathbf{G})\phi_k(\mathbf{k} + \mathbf{G}), \] (2.11)

which requires fewer terms than the simple plane wave expansion since each term has both a plane wave component and a component which oscillates rapidly near the core. Substituting these into the one-electron Schrödinger equation 2.3 gives

\[ \left\{ \frac{\hbar^2}{2m} (\mathbf{k} + \mathbf{G})^2 - E(\mathbf{k}) \right\} C_k(\mathbf{G}) + \sum_{\mathbf{G}'} W(\mathbf{G}, \mathbf{G}')C_k(\mathbf{G}') = 0. \] (2.12)

Whilst this equation is very similar to the one for simple plane waves, the matrix elements \( W(\mathbf{G}, \mathbf{G}') \) are much smaller than the equivalent \( U(\mathbf{G}, \mathbf{G}') \) elements for the plane waves. This
is due to the orthogonalisation terms partially cancelling the attraction of the nuclei. In other words, the core electrons are screening the full nuclear potential from the valence electrons.

Consider now the electron density, which as always is $\psi^*\psi$. As can be seen in figure 2.1 the wave function of a valence electron oscillates more rapidly near the core of an atom so the probability of finding the electron diminishes. This suggests that perhaps it is possible to model the atom with a weaker potential and ignore the core electrons.

![Figure 2.1: Schematic representation of how the electron wave function (top) varies near an atom (bottom).](image)

### 2.6 The Pseudopotential

If the electron in figure 2.1 was completely excluded from the vicinity of the core then it could be modelled with a simple *empty core* potential as shown in figure 2.2. Outside the cut-off radius, $r_c$, the pseudopotential exactly matches the real core potential and therefore the wave functions are correct. In reality the core electrons do not completely screen the nucleus and so the pseudopotential is non-zero within $r_c$. The aim of a good pseudopotential is to be as smooth as possible within $r_c$ and match the real potential as closely as possible outwith.

In order to understand better what form a pseudopotential has and how pseudopotentials are constructed, the next section considers the Phillips-Kleinman pseudopotential [83].
2.6. THE PSEUDOPOTENTIAL

Figure 2.2: An empty-core pseudopotential. Inside the cut-off radius, \( r_c \), the effective repulsive potential due to orthogonality exactly cancels the real Coulomb potential, \( -\frac{Z}{4\pi\epsilon_0 r} \).

2.6.1 Phillips-Kleinman pseudopotential

Consider a wave function which consists of a smooth nodeless function \( \xi(r) \) and contributions from some core states, \( \phi^c \):

\[
\phi(r) = \xi(r) + \sum_c a_c \phi^c(r) .
\]  
(2.13)

If \( \phi(r) \) is orthogonal to all the core wave functions then the constants \( a_c \) must be, as before,

\[
a_c = -\langle \phi^c(r) | \xi(r) \rangle .
\]  
(2.14)

Substitution of the wave functions (equation 2.13) into Schrödinger’s equation, \( H |\phi\rangle = E |\phi\rangle \), gives

\[
H |\xi\rangle + \sum_c a_c H |\phi^c\rangle = E |\xi\rangle + \sum_c E |\phi^c\rangle .
\]  
(2.15)

On defining \( H |\phi^c\rangle = E_c |\phi^c\rangle \), and substituting the expression for the constants given in equation 2.14 gives

\[
H |\xi\rangle + \sum_c (E - E_c) |\psi^c\rangle \langle \psi^c | \xi\rangle = E |\xi\rangle .
\]  
(2.16)

Finally, writing the Hamiltonian operator as the sum of kinetic and potential energy operators gives

\[
T |\xi\rangle + \left( V + \sum_c (E - E_c) |\psi^c\rangle \langle \psi^c | \right) |\xi\rangle = E |\xi\rangle .
\]  
(2.17)

The quantity in the round brackets is the pseudopotential. The second part of the pseudopotential is a sum of projection operators. Since each core state has a particular angular momentum,
the corresponding operator acts only on this angular momentum component of $|\xi\rangle$. Whilst the eigenstates $|\xi\rangle$, of equation 2.17 are pseudo wave functions, the eigenvalues are in fact the true eigenvalues of the system. Since the eigenvalues are insensitive to the actual value of $E - E_c$, the pseudopotential is not unique. Figure 2.3 shows a schematic illustration of a pseudopotential. There are many different forms of pseudopotential. Section 2.12 discusses norm-conserving non-local and ultra-soft pseudopotentials, both of which have been used in calculations for this thesis.

![Image]

Figure 2.3: A schematic representation of a pseudopotential $U(r)$. The Coulomb repulsion $V(r) \propto r^{-1}$ is also shown for comparison. $r_c$ is the cut-off radius of the potential.

## 2.7 Muffin Tin Approximation

The Muffin Tin approximation [17] ultimately has the same goals as the pseudopotential method: both want to simplify the interactions between valence electrons and the ionic core so as to increase the speed and viability of calculations without compromising accuracy. Their methods of achieving this aim are however quite different.

In the Muffin Tin approximation the external potential is assumed to be spherically symmetric within some radius (the Muffin Tin Radius!) and constant outside this radius. It is then natural to use basis functions which have a spherically symmetric form within the radius, coupled to a plane wave tail outside. Such basis functions are known as augmented plane waves and offer another efficient basis set for expanding the valence wave functions.
2.8 Calculation of the electron density

The use of pseudopotentials as described above presents a problem for carrying out calculations: In order to calculate the wave functions it is necessary to know what the potential energy operator $V$ is. However, this operator includes the electron-electron interactions and therefore in order to determine $V$ it is necessary to first know what the wave functions are. Exactly what these electron-electron interactions are will be discussed later in section 2.9.

This problem may be overcome as illustrated in figure 2.4. Start by guessing an electron density, $n(r)$. The superposition of electron densities of free atoms may be suitable. With this electron density it is possible to calculate the potential $V$ and hence the wave functions. It is then a simple matter to construct the new electron density from the wave functions. If the old and the new densities are the same, then we have the correct ground state electron den-

![Flow diagram depicting the iterative process to determine the ground state electron density](image-url)
More likely however, they will differ, in which case the old and the new densities need to be combined to produce another electron density and the process continues. When the two electron densities finally become equal, self-consistency is said to have been achieved and the process is complete. This is the ground state electron density.

### 2.9 Electron-Electron Interactions

In section 2.2 the decoupling of the motion of the electrons from the motion of the ions was discussed. Further, we have seen the form of a simple pseudopotential and discussed how to solve Schrödinger’s equation self-consistently. However, up to this point the treatment of the interactions of electrons has largely been ignored. The problem is that including all the interactions explicitly is a many-body problem which is insolvable. We therefore need a method which will reduce the many-body equation to a set of one-electron equations without losing the essence of the interactions which include not only Coulombic repulsions but also the correct exchange and correlation interactions. The development of such methods was a major breakthrough towards the end of the last millennium. One of the simplest methods is the Hartree approximation and this will be discussed first before considering the techniques actually used in this work, namely density functional theory, and the local density and generalised gradient approximations.

#### 2.9.1 The Hartree Approximations

Under the Hartree Approximation [17] all electrons are treated as independent, non-interacting particles. The wave functions of these electrons are solutions to the one-electron Schrödinger equation:

$$\frac{-\hbar^2}{2m} \nabla^2 \psi_i(r) + (V_N + V_H) \psi_i(r) = E_i \psi_i(r)$$  \hspace{1cm} (2.18)

where the potential due to the ions having charge $Z_I$ felt by the electrons is:

$$V_N = \sum_I \frac{Z_I e^2}{4\pi\varepsilon_0 |r - R_I|}.$$

\hspace{1cm} (2.19)
The electron-electron interaction is not totally neglected, instead the electron is said to be interacting with the total charge density, $\rho(r)$. This interaction is described by the Hartree potential

$$V_H = \frac{e^4}{4\pi\epsilon_0} \int \frac{\rho(r')}{|r - r'|} \, dr'.$$  \hspace{1cm} (2.20)

The problem with the Hartree approximation is two-fold. Firstly, since an electron interacts with the total charge density, it does in effect, interact with itself. This is not only physically nonsensical but also violates Pauli’s exclusion principle since effectively there are two electrons with the same spin in the same place at the same time. However, this is not too bad in a free electron solid in which each calculated wave function represents in the order of $10^{23}$ electrons and each electron correctly interacts with the other $10^{23} - 1$ electrons but the resulting description of strongly correlated systems in which the electrons are localised on individual atoms is inaccurate. Secondly, since the electrons are independent, we may write the full wave function as the product of the one-electron wave-functions [88]:

$$\Psi(r_1, r_2, ..., r_N) = \prod_{i=1}^{N} \psi_i(r_i).$$  \hspace{1cm} (2.21)

This is insensitive to the order of the one-electron wave functions. Since electrons are fermions, $\Psi$ should be anti-symmetric under the exchange of electrons; that is, the sign of $\Psi$ should depend on the order of the one-electron wave functions in the last equation. As a result the Hartree approximation violates Fermi-spin statistics.

The Hartree-Fock approximation overcomes the violation of Fermi spin statistics by writing the full wave function as the Slater determinant of a matrix of one electron wave functions [56]:

$$\Psi(r_1, r_2, ..., r_N) = \begin{vmatrix} \psi_1(r_1) & \psi_1(r_2) & \cdots & \psi_1(r_N) \\ \psi_2(r_1) & \psi_2(r_2) & \cdots & \psi_2(r_N) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_N(r_1) & \psi_N(r_2) & \cdots & \psi_N(r_N) \end{vmatrix}.$$  \hspace{1cm} (2.22)

The Hartree-Fock approximation adds another repulsive term which acts only between electrons of the same spin. In this way, electrons with the same spin are excluded from the vicinity of each other and so Pauli’s exclusion principle is satisfied.
The Coulomb repulsion between electrons is known as the \textit{Coulomb correlation} and should prevent any two electrons getting too close. However, since under the Hartree approximations an electron only interacts with an averaged charge density and not with individual electrons this Coulomb correlation is completely ignored.

\section*{2.10 Density Functional Theory}

A breakthrough in the calculation of the electronic properties of materials came in 1964 when Hohenberg and Kohn proved a theorem \[38\] concerning the motion of electrons in an \textit{external potential} due to atomic cores. The theorem states

\begin{quote}
All properties of a system, including the total energy, involving interacting electrons in their ground state subject to an external potential \(V(r)\) may be expressed as unique functionals of only the electron density \(n(r)\).
\end{quote}

They also proved that the electron density which minimises the total energy is the ground state density. The problem therefore is reduced to the variational problem of minimising the total energy. The total energy of the system may be written exactly:

\[E[n(r)] = \int V_{\text{ext}}(r)n(r) \, dr + \frac{e^2}{2} \int\int \frac{n(r)n(r')}{4\pi\varepsilon_0 |r-r'|} \, dr \, dr' + G[n(r)] \quad (2.23)\]

where \(G[n(r)]\) is a universal function of the electron density. The form of the functional however, is unknown. This theorem is also only valid for the ground state of a system; unfortunately it is not valid for excited states.

The above theorem on its own is still insufficient since the functional \(G[n(r)]\) is unknown. The next breakthrough came a year later when Kohn and Sham \[47\] rearranged Schrödinger’s equation as a set of exact, coupled one-electron equations. Thus the electrons move independently of each other except that they are subjected to an effective potential which emulates their interactions with the other electrons. Kohn and Sham demonstrated that this effective potential is a unique functional of the electron density. The resulting set of equations representing these \textit{pseudo electrons} are known as the Kohn-Sham equations.

\[-\frac{\hbar^2}{2m} \nabla^2 \psi_i(r) + V_{\text{eff}} \psi_i(r) = E_i \psi_i(r) \quad (2.24)\]
where
\[ V_{\text{eff}} = V_{\text{ext}}(r) + \int \frac{n(r')e^2}{4\pi\epsilon_0|r - r'|} \, dr' + \mu_{XC} \] (2.25)

and
\[ n(r) = \sum_i \psi_i^*(r)\psi_i(r) . \] (2.26)

The \( \mu_{XC} \) in equation 2.25 incorporates all the exchange and correlation effects. It is the derivative of the exchange and correlation energy. Once an initial set of wave functions have been guessed, the Kohn-Sham equations (2.24-2.26) may be solved iteratively to give the Kohn-Sham eigenvalues. Strictly these eigenvalues are no longer the true eigenvalues but the electron density is the correct ground state density. Unfortunately, the actual form of the exchange and correlation energy is unknown so we have to revert to approximations in order to do the calculations!

### 2.11 Approximations

Although the exchange and correlation term in equation 2.25 is in general unknown, the ground-state energy for a homogeneous electron gas, jellium, has been calculated by Nozieres and Pines \[66\] and may be written:
\[ E_0 = E_{\text{kin}} + E_X + E_C = \frac{30.056}{R_s^2} - \frac{12.458}{R_s} + (0.4216 \ln R_s - 1.564) \quad [\text{eV}] . \] (2.27)

The first two terms correspond to the kinetic and exchange energies as calculated by the Hartree-Fock scheme. The final term is the correlation energy according to Nozieres and Pines. The constant \( R_s \) is the radius of the sphere of charge containing on average one electron. The charge density, \( \rho \), is then simply \( (\frac{4}{3}\pi R_s^3)^{-1} \). This equation is known to be a good description of the ground state for charge densities corresponding to \( R_s \) between 2 and 6 nm. The typical electron density of metals falls within this range.

#### 2.11.1 The Local Density Approximation

In real atomic systems the electron density is far from homogeneous as the ions cause large disturbances. It is therefore not possible to use the result of Nozieres and Pines, equation 2.27,
directly. However, the local density approximation (LDA) employs it to calculate the exchange and correlation energy of real systems. The method was developed in 1965 by Kohn and Sham [47] and by Schülter and Sham [76] and has been used very successfully to accurately model a wide range of systems.

Under the LDA the exchange and correlation of a small element of charge is assumed to be the same as that of the same amount of jellium with the same density. The exchange and correlation energy for the whole system may thus be written

$$E_{XC}[n(r)] = \int \mathcal{E}_{XC}(n(r)) n(r) \, d(r) , \quad (2.28)$$

The exchange and correlation energy does not appear as such in the Kohn-Sham equations (2.24-2.26) but instead as a potential. This potential is simply the derivative of the exchange and correlation energy:

$$\mu_{XC}[n(r)] = \frac{\delta E_{XC}[n(r)]}{\delta n(r)} = \frac{\partial [nE_{XC}]}{\partial n} . \quad (2.29)$$

The problem with the Hartree approximation was that the electron effectively interacted with itself and that Fermi spin statistics were violated. The Hartree-Fock approximation deals with the exchange of electrons of the same spin according to the Pauli exclusion principle. However, there is no such restriction on electrons of opposing spins. The electron distribution in the Hartree-Fock approximation therefore incorrectly depends on the direction of the spin of the electrons. The Coulomb correlation between electrons in real life is independent of spin and is thus ignored by both approximations. Thus the LDA offers very significant improvements over the Hartree and Hartree-Fock methods. Figure 2.5 compares the electron density close to an electron under the three approximations. The local spin density approximation, which is the closest to reality, is also shown.

While the exchange and correlation hole around an electron in the LDA may not be exactly the right shape it does correctly correspond to the charge of exactly one electron. In its standard form the LDA treats spin up and spin down electrons identically. Often this is sufficient and accurate results may be obtained. If the system is magnetic however, the local spin density approximation (LSDA) which treats spin up and spin down electrons independently must be used.
2.11. APPROXIMATIONS

Despite initial scepticism the LDA has been used very successfully. The LDA however, tends to under-bind the core electrons of a system while over-binding the atoms within a solid or molecule. Calculated properties such as absorption spectra therefore are determined less accurately than we might wish. For this reason there have been several attempts to improve the LDA by including not only a dependence on the electron density but also on the derivatives of the electron density. These extensions are known as generalised gradient approximations.

2.11.2 The Generalised Gradient Approximation

There have been several attempts to produce generalised gradient approximations (GGAs). The exchange and correlation energy functionals have the form:

\[
E_{XC}[n(r)] = \int f(n(r), \nabla(n)) \, d(r)
\]  

(2.30)

Perhaps the best [69], and certainly the one employed in this work, is Perdew and Wang’s second attempt [70, 68].
2.12 Pseudopotentials

The choice of pseudopotential is very important in the accurate description of the properties of systems. Ideally the pseudo wave-function should have no nodes within a certain cut-off radius $r_c$. Outwith this radius the pseudo wave-function should be identical to the real wave function. The pseudo charge density should then also be the same as the real charge density outwith this radius. The pseudopotential is built so that the pseudo wave-functions match exactly the real wave functions at $r_c$. Usually the equality of their first and often the second derivatives is also enforced. To generate a pseudopotential the full Schrödinger equation is solved for all electrons in an isolated atom. After smoothing the valence wave functions inside the core radius, the Schrödinger equation may be inverted to give the pseudopotential.

Good pseudopotentials should reproduce the scattering properties of the atom at as large a range of energies as possible. By ensuring that the correct amount of charge is enclosed within the core, the correct Coulomb potential outside is obtained. This helps to minimise the error in the scattering properties. Pseudopotentials which are made to have the correct amount of charge within the core are said to be norm conserving [30].

2.12.1 Non-local pseudopotentials

Section 2.6.1 introduced the Phillips-Kleinman pseudopotential in order to illustrate the general form of pseudopotentials. In principle, equation 2.17 represents a perfectly good pseudopotential, however, it requires the evaluation of a matrix of the form $\langle \psi' | \phi^c \rangle \langle \phi^c | \psi \rangle$. To do this, the value of an integral for each pair of plane waves must be calculated. Since the number of plane waves is typically of order $10^3 - 10^4$ or higher and as $N_{pw}(N_{pw}+1)/2$ integrations are needed, this method is computationally infeasible.

The Kleinman-Bylander [46] pseudopotential solves this problem by splitting the pseudopotential into two parts. The pseudopotential consists of an arbitrary local potential which is felt by the whole wave function and a non-local part which describes the difference between this local potential and the pseudopotential which each angular momentum component of the wave function should experience. The local part is best chosen so as to minimise the differences
between the most common angular momentum of the pseudopotential and the local part. If this difference for the angular momentum component $l$ is written:

$$\delta_l = V_l - V_{local}$$  \hspace{1cm} (2.31)$$

then the Kleinman-Bylander pseudopotential may be written:

$$V_{KB} = V_{local} + \sum_{lm} |\phi_{lm}^0 \delta V_l \rangle \langle \phi_{lm}^0 | \delta V_l | \phi_{lm}^0 \rangle .$$  \hspace{1cm} (2.32)$$

This is better than the Phillips-Kleinman pseudopotential since it involves only separable integrals of the form $\langle \phi_{lm}^0 | e^{\mathbf{G} \cdot \mathbf{r}} | \phi_{lm}^0 \rangle$. The number of integrals which need to be evaluated is now $N_{pw}$. The above equation is however, strictly only correct for the eigenstate with which it was created. There is nothing to say that it will be of any use for modelling other systems. This is the problem of transferability of pseudopotentials. For this reason, the accuracy of any new pseudopotential must be carefully checked under a wide variety of conditions. If the electronic configuration of the system of interest is sufficiently close to the reference state then the pseudopotential should work. It has proved very difficult however to build pseudopotentials for systems containing highly localised valence orbitals such as first-row transition-metals. Further, the norm conserving requirement causes problems for other important elements such as nickel and oxygen. In this work, the norm conserving potentials supplied with CASTEP were unable to accurately model the behaviour of the guest atoms in the hotel structure. Consequently, the majority of the calculations done in this work used ultra-soft pseudopotentials.

### 2.12.2 Ultra-soft pseudopotentials.

The potentials used in the calculations reported in this thesis were in general those of the ultra-soft variety distributed with VASP.

Ultra-soft pseudopotentials were originally proposed by Vanderbilt [85]. As mentioned above good norm-conserving pseudopotentials can be hard to make for some elements and then the large number of plane waves required in the calculations makes them computationally expensive. For nickel and oxygen the pseudo wave-functions are not much smoother than the all-electron wave function. Since there is no norm-conserving constraint in ultra-soft pseudopotential theory, the ultra-soft pseudopotentials may be optimized for smoothness within the
core region. The charge deficit within the core due to this extra smoothing is replaced by extra charges localised on the centres of the atoms. In creation, the ultra-soft pseudopotentials are fitted to several electronic configurations. In this way the scattering properties and their energetic derivatives are correct at several energies spanning the range of occupied states. By including more reference states in the fitting procedure the scattering properties and hence the transferability of the pseudopotential may be systematically increased.

The generation of ultra-soft pseudopotentials basically creates Kleinman-Bylander separable pseudopotentials for each electronic configuration [55]. Thus, the ultra-soft pseudopotentials have multiple projection operators for each angular momentum component. Which operator is actually used depends on the system and hence the pseudopotential becomes part of the self-consistent process. The transferability is further improved by treating the shallow core electrons as valence electrons. However, since this increases the number of electrons in the calculation, so it decreases the computational efficiency.

2.13 Practicalities

So far we have discussed the theoretical background to ab initio calculations. However, in order to use these techniques in practice we need to consider a few practicalities such as how to calculate the electron density from the wave functions numerically, where to truncate the series expansions and how to study complex systems. First consider the numerical calculation of the wave functions.

2.13.1 k-point sampling

In earlier sections we have mentioned how the electron density $n(r)$ may be easily calculated from the wave functions. The electron density is given by

$$n(r) = \frac{v}{(2\pi)^3} \int_{BZ} \sum_j \psi_j^* \psi_j \, dk$$

(2.33)

where the integral is over the Brillouin zone and $v$ is the volume of the cell. Whilst it is easy to write this mathematically, in practice the integral is too difficult to evaluate exactly so it needs
2.13. PRACTICALITIES

to be evaluated numerically. Fortunately the electron wave functions vary smoothly throughout
the Brillouin Zone so the integral may be approximated with a sum which may be sampled at
a few discrete \( k \)-points. If each \( k \)-point is assigned a weight \( \alpha_i \) such that \( \sum_i \alpha_i = 1 \) then the
electron density may be written

\[
 n(r) = \sum_i \alpha_i \sum_j \psi_{j,k_i}^* \psi_{j,k_i} \tag{2.34}
\]

There are several schemes for choosing which \( k \)-points to include in the sum. The most com-
mon scheme, which is used here, is that of Monkhorst and Pack [57]. Under the Monkhorst-
Pack scheme the Brillouin Zone is divided up into equally sized cuboids. The \( k \)-points included
in the sum are those at the centres of each of these cuboids. In molecular systems the wave
functions vary very slowly, if at all, through the Brillouin Zone so the sum need only contain
one \( k \)-point, the \( \Gamma \) point which is at the centre of the Brillouin Zone. In metals however the
bands sometimes vary dramatically, particularly near the Fermi surface, and so many more
\( k \)-points are required. Fortunately in many systems, several \( k \)-points may be equivalent by
symmetry hence the number of terms in the sum may be reduced without any loss of accuracy.
The smallest portion of the Brillouin Zone which can completely describe the whole Brillouin
Zone with the help of symmetry is called the irreducible Brillouin Zone. The smallest set of
\( k \)-points contains only those which lie in the irreducible Brillouin Zone.

Clearly, the smaller the number of \( k \)-points which need to be included in the sum the quicker
the calculations will be. However, particularly with metals, if an insufficient number are in-
cluded then the results will be inaccurate. It is therefore necessary to carry out convergence
tests to determine the mesh size to be used. Whereas the total energy of a system tends asymp-
totically towards the true value as the cut-off energy is increased, while the number of \( k \)-points
is increased, the total energy tends to oscillate around the true value, see figure 2.6.

2.13.2 Fermi level effects

The occupation of energy bands is governed by the Fermi energy. In insulators the bands either
have a lower or a higher energy and therefore are either full or empty respectively. There is
also a band gap between the full and empty bands. In metals however bands cross the Fermi
energy and so are filled in some parts of the Brillouin Zone and not in others. It is therefore vital to accurately know the Fermi energy. To account for this discontinuity, equation 2.34 may be rewritten as

$$n(r) = \sum_i \alpha_i \sum_j \psi_{j,k_i}^* \psi_{j,k_i} \Theta(E_f - E)$$

(2.35)

where $\Theta(E_f - E)$ is the step function, $E_f$ is the Fermi energy and $E$ is the band energy. This equation converges very slowly with respect to the number of k-points. Consequently, for accurate results it is necessary to use lots of k-points, particularly in metals. However, since doubling the number of k-points doubles the amount of memory required for the calculations, it is advantageous to improve the rate of convergence by other methods.

One solution is to effectively increase the number of k-points by interpolation. The linear tetrahedron method interpolates the band energies in a tetrahedron made by 4 k-points. The method is improved by the addition of Blöchl corrections which add 2nd order terms to the interpolation. However, the forces derived from such calculations are not so accurate if the bands are only partially full. If the structures of metallic systems are to be relaxed then it is better to replace the step function in equation 2.35 with a smooth function.

One possibility is to replace the step function with a Fermi-Dirac type distribution. However, whilst this significantly improves the convergence of the sum it produces the wrong answer. In
the limit that the smearing width $\sigma$, tends to 0, then the correct answer is recovered. Methfessel and Paxton [54] adopt a more sophisticated approach in which they expand the step function in terms of a series of Hermite polynomials. The zeroth order term is the same function as used for Gaussian smearing:

$$S_0(x) = \frac{1}{2} \left(1 - \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} \, dt\right)$$  \quad (2.36)

where $x = \frac{E - E_f}{\sigma}$. The $N^{th}$ order Methfessel-Paxton approximation to the step function is:

$$S_N(x) = S_0(x) + \sum_{n=1}^N A_n H_{2n-1}(x) e^{-x^2}.$$  \quad (2.37)

The Hermite polynomials are given by the following recurrence relations

$$H_0(x) = 1, \quad H_1(x) = 2x,$$  \quad (2.38)

$$H_{n+1}(x) = 2x H_n(x) - 2n H_{n-1}(x).$$  \quad (2.39)

### 2.13.3 Crystal distortions

Crystal structures are generally highly symmetric. However, sometimes it is energetically favourable to reduce the amount of symmetry in the system. According to the theorem of Jahn and Teller [], any non-linear structure with a degenerate electron configuration will distort to remove the degeneracy. If there is an odd number of electrons, Kramer’s rule states that the ground state must be doubly degenerate. The crystal will only distort according to Jahn and Teller’s theorem if it will not break Kramer’s rule. The magnitude of any distortion is not necessarily sufficiently large to be observable. Jahn-Teller distortions are responsible for some of the octahedral based structures of some transition metal compounds. For example, Cu$^{2+}$ ions are often found at the centre of distorted octahedra with four short bonds and two long bonds [90]. The magnitude of the distortion depends on the constituents of the compound. In CuF$_2$ the distortion is fairly small. CuO has an almost planar structure because the distortions are so large.

Alternatively, some systems with a half filled band can undergo a Peierls type distortion [] and behave as one dimensional metals. The distortion of crystal splits the half filled band into two. The second band is then partially occupied due to thermal excitations and the system has metallic properties. At zero Kelvin however, the system is insulating.
2.14 Molecular Dynamics

Molecular dynamics techniques allow the evolution of systems at finite temperature to be studied in a way which is surprisingly similar to real experiments [24]. In both cases the sample to be studied is prepared and allowed to equilibrate before any measurements are made. The properties which can be measured are statistical in nature and so fluctuate. In order to obtain accurate results therefore it is desirable in both cases to average over long time periods of time.

The theoretical system evolves with time according to Newton’s equations of motion. As the ions are large, it is generally assumed that the behaviour is purely classical in nature. Once the forces have been calculated (see section 2.14.1) the equations of motion can be integrated. Often the molecular dynamics simulations use the Verlet algorithm for the integration. This has the advantage of good energy conservation over long periods of time but at the expense of a loss of short term accuracy. The Verlet algorithm uses the positions of the particles at times $t$ and $t - \Delta t$ and the forces on the particles at time $t$ to predict the positions at time $t + \Delta t$. An improvement on the Verlet algorithm is known as the velocity Verlet method which uses the positions, velocities and forces at one time to compute the positions a short time later. However, only once these new positions are known and the new forces calculated is it possible to calculate the new velocities. The ab initio program VASP however uses a predictor-corrector algorithm. The fifth order version of this algorithm uses information about the current positions and the first four derivatives to determine the predicted new position. The forces at this new position are then calculated and hence the values of the derivatives. These values are then used to correct the predicted position. This procedure could be iterated to find the correct position of the particles, however this would consume significant amounts of time for only a small increase in accuracy. In fact, it would be more productive to use a shorter time step as the error of the $n^\text{th}$ order algorithm is of order $\Delta t^n$.

To do experiments at constant temperature, the system to be studied is placed in contact with some form of a heat bath. In molecular dynamics simulations the effect of the heat bath is replaced by some mechanism for regulating the temperature. Before doing simulations however, it is necessary to have a measure of the temperature of the simulation. A convenient definition
in terms of the average kinetic energy per atom is

\[ \left\langle \frac{1}{2} m v^2 \right\rangle = \frac{3}{2} k_B T. \]  \hspace{1cm} (2.40)

However, the centre of mass of the system is fixed, so in practice there are only 3N-3 degrees of freedom in a system of N atoms and \( k_B T \) is therefore twice the total kinetic energy divided by 3N-3. A simple solution is to scale the velocities at each time step and so force the correct temperature on the system. This however leads to un-physical results. The temperature of a real system is actually a statistical entity and is not perfectly constant but fluctuates with a variance of 2/3N. Such behaviour may be reproduced in simulations with the aid of a thermostat. Anderson [24] suggested replacing the experimental heat bath with stochastic impulses which act randomly on selected particles. Between impulses, the system evolves normally according to Newton’s equations of motion. The so-called Anderson thermostat produces a true canonical ensemble but unfortunately the trajectories of the particles are not very realistic.

Another scheme which produces a canonical ensemble and also realistic trajectories is that proposed by Nosé [65]. The Nosé thermostat introduces an extra coordinate \( s \) into the Lagrangian of the system. This extra coordinate along with an associated “mass” then controls the motion of the temperature. This is an example of the extended Lagrangian technique which has found a wide range of uses. As well as studying systems at constant temperature it can also be used to study systems at constant pressure by introducing fictitious coordinates and masses for the basis vectors of the supercell. However, this is problematic in \textit{ab initio} programs due to the previously mentioned problems associated with plane wave cut-offs and supercell sizes. Car and Parrinello [12] used the extended Lagrangian technique to revolutionise \textit{ab initio} molecular dynamics. By associating masses with the plane wave coefficients and introducing a damping factor, Car and Parrinello could determine the coefficients of the plane waves in the ground state wave function.

### 2.14.1 Forces

In order to do molecular dynamics simulations it is necessary to evaluate the forces acting on the ions in the system. The ability to determine the forces is also critical in determining the
ground state structure of a system. Quite generally, the force on atom $I$ which has position vector $\mathbf{R}_I$ is

$$f_I = -\frac{dE}{d\mathbf{R}_I}. \quad (2.41)$$

As an ion moves around, the wave functions change as well as the energy of the system. The force on atom $I$ may therefore be written:

$$f_I = -\frac{\partial E}{\partial \mathbf{R}_I} - \sum_i \frac{\partial E}{\partial \psi_i} \frac{d\psi_i}{d\mathbf{R}_I} - \sum_i \frac{\partial E}{\partial \psi_i^*} \frac{d\psi_i^*}{d\mathbf{R}_I}. \quad (2.42)$$

If the wave functions are eigenstates of the Hamiltonian, the final two terms combine to give zero, since $E = \sum_i \langle \psi_i | H | \psi_i \rangle$ it follows that $\partial E/\partial \psi_i^* = H | \psi_i \rangle$. The last two terms may then be written as [67]

$$\sum_i \langle \frac{\partial \psi_i}{\partial \mathbf{R}_I} | \lambda_i | \psi_i \rangle + \sum_i \langle \lambda_i | \frac{\partial \psi_i}{\partial \mathbf{R}_I} \rangle = \sum_i \lambda_i \frac{\partial}{\partial \mathbf{R}_I} \langle \psi_i | \psi_i \rangle, \quad (2.43)$$

where $\lambda_i = H | \psi_i \rangle$. As $\langle \psi_i | \psi_i \rangle$ is just the normalisation constant its derivative is zero. The force on atom $I$ is therefore simply

$$f_I = -\frac{\partial E}{\partial \mathbf{R}_I}. \quad (2.44)$$

This is the Hellmann-Feynman theorem [21]. In density functional theory, the energy is an explicit functional of only the charge density and not of the individual wave functions. The Hellmann-Feynman theorem therefore allows the computation of the forces on the ions from only the charge density without the need to know the individual wave functions.

The errors in the forces calculated with the Hellmann-Feynman theorem are directly proportional to the errors in the wave functions. In contrast, the error in the total energy is second order with respect to errors in the wave functions [2]. It is therefore much more difficult to accurately calculate the forces than it is to calculate the total energy; many more plane waves are needed in the expansion of the wave functions. The derivatives of the wave functions with respect to the ionic positions in equation 2.42 can be further split to show the dependence on the basis functions. The resulting contribution to the force from the basis set is known as the Pulay force. If however, a plane-wave basis set is used, the basis functions are independent of the positions of the ions and so the Pulay force on the ions is zero.
If the volume of the cell is changed during a calculation and the number of plane waves in the basis set is kept constant, then the cut-off energy of the basis set will vary. The resulting stress on the basis vectors due to the change in cut-off energy is the Pulay stress. If the basis set is sufficiently large so that the total energies are converged with respect to the number of plane waves, then varying the cut-off slightly will have no effect on the total energy and the Pulay stress is zero. If however, the basis set is not sufficiently large the Pulay stress on the cell will be non zero. The Pulay stress on the cell are independent of the positions of the ions. It is therefore possible to calculate the Pulay stress once for each cell [67]. The results Pulay correction may then be added as an external pressure [88].

### 2.14.2 Plane-wave cut-off

In order to reduce computing resources and time required to solve Schrödinger’s equation it is desirable to use as few plane waves as possible in the expansion of the wave functions. However, if an insufficient number is used then the calculated properties will be inaccurate. The series contains all the plane waves whose kinetic energy $\hbar^2|\mathbf{k} + \mathbf{G}|^2/2m_e$ is less than a specified maximum, $E_c$. As the cut-off is increased the total energy of the system decreases asymptotically to the true value, see figure 2.7. The number of plane waves whose energy is below the cut-off energy depends on the volume of the cell. The smaller the cell the smaller the number of plane waves, this can lead to problems if the cell volume is being relaxed since the wave vector of the plane waves varies as the volume of the cell changes and hence so does the effective cut-off.

Before doing any accurate calculations it is therefore imperative to ensure that the plane wave cut-off is set sufficiently high. In the calculations of the properties of metals presented in this thesis it was found that a cut-off energy of 350 eV was generally sufficient to converge the ground state total energy to within 1 meV per atom.

When comparing the stability of two structures it is not always necessary to have absolute convergence of the total energy with respect to the number of plane waves. Including higher energy plane waves improves the description of the core region of the atoms. The electrons in the core are in general not involved in the bonding and so increasing the number of high energy
plane waves tends to have the same effect in each structure. The difference in energy between two structures therefore converges faster than the total energy. Further, if the calculations of the energies of the two structures are done with the same cut-off energy, then the errors in both calculations due to the truncations of the series will be similar and may therefore be ignored.

2.14.3 Determination of electron types

Using plane wave expansions of the wave functions, as in real life, it is not possible to accurately know on which atom each electron is. However, qualitative answers may be obtained by projecting the wave functions on to spherical harmonics centred upon each atom if they are within a certain distance of the atom. This distance is the Wigner-Seitz radius and in simple systems containing only one species then it can be easily calculated so that the total volume of the spheres is equal to the volume of the system. In systems with several species, the choice of the Wigner-Seitz radii becomes more difficult. In the hotel structure, the choice is even more unclear since the host-guest separation may on occasion become very small such that there will be a large overlap of the spheres. However, since all the atoms are of the same type then only one radius may be specified. For want of a better solution, the radius chosen gives a total
volume equal to that of the system.

2.14.4 Strategy for determining relaxed structures

The *ab initio* programs, VASP and CASTEP, allow both the cell parameters and all the ionic degrees of freedom to relax simultaneously thereby immediately giving the relaxed structure. However, there are several disadvantages to allowing the programs to do everything at once. Firstly, for large complicated structures there are lots of small local minima in which the minimisation routines may become stuck while looking for the global minimum. Also, VASP and CASTEP expand the Kohn-Sham equations in terms of a fixed number of plane waves. If the volume of the sample changes, then the wavelengths and hence the energies of the waves change. This is not such a problem if the volume decreases since the energies will increase and so will the cut-off energy of the series, thereby increasing the accuracy of the calculation. However, if the volume increases then the cut-off will decrease and so will the accuracy of the calculation. The best tactic is to keep the volume fixed during a relaxation and anneal it manually. While this requires more work it has the advantage that all calculations are executed with the same cut-off and therefore all calculations should be equally well converged and any errors will be systematic and hence the same for all. Also, if the total energy is sufficiently well converged with respect to the plane wave cut-off, small variations in the cut-off energy should not make much difference to the final answer. The equilibrium volume may also be found by fitting results from several calculations to a Murnaghan equation of state, see section 2.14.6.

2.14.5 More Complicated Systems

In section 2.3 and subsequent sections the theory was developed on the grounds that the system was periodic and monatomic. However, even if this is not the case then it is often still possible to do some calculations. By creating a larger cell which contains several particles, it is possible to model most systems. Such a cell is known as a supercell. If a system is a solid with several different species of atoms, then the choice of supercell is quite simple. The interesting question is how to deal with solids which have impurities, surfaces or even liquids and molecules. Strictly speaking the study of such systems is impossible since periodic boundary conditions
Figure 2.8: a) If a single molecule is placed in a sufficiently large supercell the interactions between neighbouring molecules will be negligible and hence the calculated properties will be those of an isolated molecule. b) A supercell for calculating the properties of surfaces. There needs to be enough layers of atoms in the slab so that the atoms in the middle do not feel the effect of the surface. Also, the supercell needs to be sufficiently tall that the top and bottom surfaces do not interact with each other through the vacuum.

are enforced. However, by judicious choice of supercell very good results may be obtained. In all cases, the larger the supercell employed the better the results are.

Consider an isolated molecule. Using the methods describe above, what is actually studied is an infinite system of regularly spaced molecules, see figure 2.8. If the distance between molecules (which depends on the size of the supercell) is sufficiently large, then neighbouring molecules may be assumed not to interact and hence the calculated properties may be taken to be those of an isolated molecule. The box is sufficiently large when the properties cease changing as the size of the box is increased [67]. There are also other methods embodied by different programs which are more suited to the calculation of the properties of isolated molecules [26]. However, they are unable to study processes such as the absorption of molecules on to surfaces.

Surfaces may be studied by considering a large box containing a slab of atoms. The slab is generally infinite in two dimensions. It needs to be sufficiently thick so that the atoms in the middle believe they are in an infinite solid and so that the top and bottom surfaces do not affect each other through the slab. Further, the cell must be sufficiently tall so that there is no interaction between surfaces through the vacuum. See figure 2.8.
Finally, the study of liquids and impurities simply requires a large supercell containing many atoms so that an atom does not interact with its image through the periodic boundary conditions. In the case of studying the impurities, even though there may be only one impurity in the supercell, the system has an infinite number of them regularly repeating throughout the crystal. Therefore, larger supercells allow systems with lower concentrations of impurities to be studied.

2.14.6 Murnaghan Equation of State

When an element or compound is being studied, it is often desirable to know how the energy varies with volume. For example, if we look at two possible structures for a substance, the prevalent structure at a particular volume (pressure) is that which has the lowest energy (enthalpy). If the first structure has lower energy than the second at a particular volume, it will be the stable phase at that volume. If at a smaller volume, the second structure has a lower energy than the first then it will be the stable phase at that smaller volume, and there must be a phase transition somewhere in between. The pressure at which the transition occurs is given by minus the gradient of the tangent which is common to both curves, see figure 2.9. More generally, the pressure at any particular volume is given by minus the gradient of the energy-volume curve at that point.

Figure 2.9: This figure shows fitted Murnaghan equation of states for two competing structures. The straight line is simultaneously tangential to both curves and hence its gradient is the transition pressure from one to the other.
The determination of transition pressures by finding the gradient of the common tangent is simpler and more accurate if functional forms for the curves are known. One function which may be used is the Birch-Murnaghan equation of state [60]:

\[
E = \frac{B_0 V}{B'_0} \left[ \left( \frac{V}{V_0} \right)^{B'_0} - 1 + 1 \right] + E_0 - \frac{B_0 V_0}{B'_0} - 1
\]  

(2.45)

where \( E_0 \) is the minimum energy, \( V_0 \) is the corresponding volume, and \( B_0 \) and \( B'_0 \) are the bulk modulus and its derivative respectively.

One advantage of using this particular function is that it explicitly gives the equilibrium (minimum) energy for the structure and the corresponding volume and bulk modulus, and therefore facilitates comparisons between the calculations and the experimental results. The Murnaghan equation of state was fitted to the calculated energies using an existing program [88].

2.15 Summary

This chapter has briefly outlined the theory behind the \textit{ab initio} calculations which form the majority of calculations presented in this thesis. Over the last 10 to 20 years significant effort has been spent on developing efficient computer programs which implement the techniques described. Most of the \textit{ab initio} calculations presented in this thesis were executed with the Vienna \textit{ab initio} simulation package (VASP) []. Some work was also done using the Cambridge serial total energy package (CASTEP) []. As computers have become more and more powerful, so the demands made of them become greater. As a result, both codes are run both locally on ordinary serial machines, and on parallel super computers at both the Edinburgh Parallel Computing Centre and the Computing Services for Academic Research in Manchester.
Chapter 3

Vibrational Properties

The vibrational properties of a crystal determine many of its macroscopic properties such as its specific heat capacity and the velocity of sound within it. In this section we will review the formalisms that can be used to describe lattice dynamics and then explain how they can be applied to our ab initio calculations. The vibrational properties will then be related to the thermodynamic properties including the zero-point energy and the Gibbs free energy. Also, the ab initio calculations only look at materials at zero temperature. This is often sufficient but sometimes certain phases only occur at high temperature. In such systems there is a temperature induced phase change which cannot be studied using ordinary ab initio calculations. By determining the Helmholtz and Gibbs free energies it is possible to study the high temperature phases and ultimately produce pressure–temperature phase diagrams.

Some of the first calculations of the vibrational properties were done by Pawley [16] although the theory is generally attributed to Born [9]. With the increase in computing power they are now easier to do. However, as the focus of ab initio calculations has moved towards the study of systems of ever increasing complexity the calculations of vibrational frequencies has never become the norm. An alternative, cheaper method of calculating them is to calculate the elastic constants and then deduce the dynamical matrix [14, 78, 79].
Lattice dynamics has been explained in detail by Born [9]. Consider an infinite system divided into primitive cells, labelled \( l \). The atoms within each primitive cell are labelled with \( k \) from 1 to \( n \), the number of atoms in the primitive cell. Further, let each atom be displaced from their equilibrium position by a small displacement \( u_{(l)}^{(k)} \). The absolute position of each atom is then:

\[
  r_{(l)}^{(k)} = x_l + x_k + u_{(l)}^{(k)}
\]  

(3.1)

where \( x_l \) is the position of cell \( l \) with respect to some arbitrary origin, and \( x_k \) is the equilibrium position of atom \( k \) within the primitive cell.

### 3.1.1 The Harmonic Approximation

If the displacements of the atoms away from their equilibrium positions are small, the forces induced on the atoms due to these displacements may be taken as being proportional to the displacement. This linearity is assumed under the harmonic approximation. Defining \( \Phi \) to be the force constant matrix we can write

\[
  f_{(l)}^{(k)} = \sum_{l'} \sum_{k'} \Phi_{(l)}^{(l')}(l_{(k')}) u_{(l')}(k')
\]  

(3.2)

where \( f_{(l)}^{(k)} \) is the force on atom \( k \) in cell \( l \) due to displacements of atoms \( k' \) in the cells \( l' \).

If there are \( N \) atoms in the system, the force constant matrix \( \Phi_{(l)}^{(l')} \) consists of \( N^2 \) separate 3×3 matrices relating the force on atom \( (l) \) to the displacement of atom \( (l') \).

Since force is minus the derivative of energy with respect to displacement and the force constant is the derivative of the force, then the force constant matrix \( \Phi \) may also be written, in component form:

\[
  \Phi_{\alpha\beta}^{(l)}(l_{(k'})} = \frac{-\partial^2 E}{\partial u_{\alpha}(l_{(k)}) \partial u_{\beta}(l'_{(k')})}
\]  

(3.3)
3.1. REVIEW OF LATTICE DYNAMICS

3.1.2 Normal Modes

A normal mode of a crystal is a permitted vibration with a specific frequency of one or more atoms about their equilibrium positions. In the harmonic approximation, the restoring force is proportional to the displacement:

\[ f(l_k) = -m_k \omega^2 u(l_k) \]  

(3.4)

where \( m_k \) is the mass of particle \( k \).

3.1.3 Mass Reduced Coordinates

The equations may be simplified by scaling the displacements by the square root of the mass of the displaced atom. These mass reduced coordinates \( \varepsilon \) are

\[ \varepsilon (l_k) = \sqrt{m_k} u(l_k). \]  

(3.5)

Thus equation 3.2 becomes

\[ f(l_k) = -\sqrt{m_k} \omega^2 \varepsilon (l_k) \]

\[ = \sum \sum \frac{1}{\sqrt{m_{k'}}} \tilde{\Phi}(l_k l' k' \varepsilon(l' k') \]  

(3.6)

Defining

\[ \mu_{kk'} = \frac{1}{\sqrt{m_k m_{k'}}} \]  

(3.7)

we then have

\[ -\omega^2 \varepsilon (l_k) = \sum \sum \mu_{kk'} \tilde{\Phi}(l_k l' \varepsilon(l' k') \]  

(3.8)

3.1.4 Periodic structures

Since the system is periodic, the oscillations of atom \( k \) in cell \( l \) differ only from those of atom \( k \) in cell \( l' \) by a phase factor

\[ \varepsilon(l_k) = \varepsilon(l' k) e^{iq(x_l - x_{l'})}. \]  

(3.9)
To simplify things further we may choose, without loss of generality, \( l' = 0 \) giving

\[
\varepsilon \begin{pmatrix} l \\ k \end{pmatrix} = \varepsilon \begin{pmatrix} 0 \\ k \end{pmatrix} e^{i\mathbf{q}.(x_l-x_0)}.
\] (3.10)

Putting this into equation 3.8 gives

\[
-\omega^2 \varepsilon \begin{pmatrix} 0 \\ k \end{pmatrix} = \sum_{l'} \sum_{k'} \mu_{kk'} \tilde{\Phi} \begin{pmatrix} 0 \\ l' \\ k \\ k' \end{pmatrix} \varepsilon \begin{pmatrix} l' \\ k' \end{pmatrix}
\]

\[
= \sum_{k'} \sum_{l'} \mu_{kk'} \tilde{\Phi} \begin{pmatrix} 0 \\ l' \\ k \\ k' \end{pmatrix} e^{i\mathbf{q}.(x_l-x_0)} \varepsilon \begin{pmatrix} 0 \\ k' \end{pmatrix}.
\] (3.11)

We can then define the Fourier-Reduced dynamical matrix as

\[
\tilde{D}(kk'|\mathbf{q}) = \sum_{l'} \mu_{kk'} \tilde{\Phi} \begin{pmatrix} 0 \\ l' \\ k \\ k' \end{pmatrix} e^{i\mathbf{q}.(x_l-x_0)}.
\] (3.12)

If there are \( n \) atoms in the primitive cell, the Fourier-Reduced dynamical matrix actually consists of \( n^2 \) separate \( 3 \times 3 \) matrices. Rather than considering it as lots of small separate matrices however, the Fourier-Reduced dynamical matrix may be viewed as one large \( 3n \times 3n \) matrix. The dynamical matrix may also be represented as one large matrix but with dimensions of \( 3N \times 3N \) where \( N \) is the total number of atoms in the system. The problem of calculating the vibrational modes is thus reduced to the solving of the \( 3n \) eigenvalue problem:

\[
-\omega^2 \xi = \tilde{D}(\mathbf{q})\xi
\] (3.13)

where \( \xi \) is a \( 3n \) dimensional vector. The eigenvectors give the modes of vibration while the eigenvalues give minus the square of the frequencies of vibration.

### 3.2 Calculating Phonons from ab initio calculations

The above expressions give the vibration modes and frequencies for an infinite system. However, while the simulated systems look infinite because of the periodic boundary conditions they are in fact finite, containing only \( l_1 \) primitive cells. Displacing an atom in the supercell is
3.2. Calculating Phonons from Ab Initio Calculations

actually moving not only it, but also all of its images throughout the infinite system. Incorporating this into equation 3.2 gives [88]

\[
f(l,k) = \sum_{l_{1}}^{\infty} \sum_{l'} \sum_{k'} \sum_{m} \Phi(l, l' + ml_{1}) u(l' + ml_{1} k')
\]

(3.14)

\[
f(l,k) = \sum_{l_{1}}^{\infty} \sum_{l'} \sum_{k'} \tilde{\Gamma}(l, l' k' k) u(l' k'),
\]

(3.15)

where \( m \) indexes all the periodic images of the supercell and \( \tilde{\Gamma}(l, l' k' k) \) is the matrix of force constants as determined from ab initio calculations of the forces. The ab initio forces include the contributions due to all the periodic images since the calculations employ periodic boundary conditions. The determination of the force constant matrix from ab initio forces is described in the next section. Using the reduced coordinates as defined before, the periodicity of the system gives

\[
\epsilon(l + ml_{1}, k) = \epsilon(l, k) e^{i\mathbf{q} \cdot (x_{l} + x_{ml_{1}} - x_{0})}
\]

(3.16)

since \( x_{l} + x_{ml_{1}} = x_{l} + x_{ml_{1}} \). These are equivalent atoms in different supercells therefore their motion is the same and in phase. This implies that

\[
e^{i\mathbf{q} \cdot x_{ml_{1}}} = 1
\]

(3.17)

\[
\Rightarrow \mathbf{q} \cdot x_{ml_{1}} = 2\pi n
\]

where \( n \in \mathbb{N} \). That is to say, only phonons whose wave vector \( \mathbf{q} \) is commensurate with the supercell may be calculated correctly.

The Fourier-reduced dynamical matrix now becomes, in component form

\[
D_{\alpha\beta}(kk'|\mathbf{q}) = \sum_{l_{1}}^{\infty} \sum_{l'} \sum_{m} \mu_{kk'} \Phi_{\alpha\beta}(0, l' k' k) e^{i\mathbf{q} \cdot (x_{l} + x_{ml_{1}} - x_{0})}
\]

(3.18)

\[
D_{\alpha\beta}(kk'|\mathbf{q}) = \sum_{l_{1}}^{\infty} \sum_{l'} \mu_{kk'} \tilde{\Gamma}_{\alpha\beta}(0, l' k' k) e^{i\mathbf{q} \cdot (x_{l} - x_{0})}
\]

and we have a \( 3nl_{1} \) dimensional eigenvalue problem similar to before;

\[
-\omega^{2} \xi = D(\mathbf{q})\xi
\]

(3.19)

with \( \mathbf{q} \cdot x_{ml} = n\pi \) for \( n \in \mathbb{N} \).
3.2.1 Calculating the force constants

Calculating the force constants is a simple, if time consuming operation. By displacing only one atom at a time, the summation signs in equation 3.15 may be dropped. Further, if the displacement is along only one axis, \( \beta \) say, then equation 3.15 becomes simply

\[
f_{\alpha}(l) = \Gamma_{\alpha\beta} \left( \begin{array}{c} l \\ l' \\ k \\ k' \end{array} \right) u_{\beta}(l').
\]

(3.20)

Some of the force constants may then be determined by simply dividing the calculated forces by the displacement. All the force constants may therefore be found by displacing each atom along each direction. Thus a total of 3N calculations need to be made to completely determine the force constant matrix. Fortunately, these calculations are relatively quick to perform since only a static calculation is necessary to evaluate the forces. Relaxing the atomic positions or the shape and size of the supercell would in fact lead to an incorrect set of forces. For many systems the number of calculations which are actually required may be significantly less than 3N due to many of the displacements and the resulting force constants being related by symmetry.

3.2.2 Application of Symmetry

When considering crystal structures it is natural to investigate the symmetries of the system. The interest in symmetry goes back a very long time; in 1669, N. Steno published a *Dissertation concerning a solid naturally contained within a solid* [82]. However, it was not until 1830 that the 32 point groups which describe all the rotational symmetries seen in real solids were first derived by Hessel [37]. The cubic point group has a total of 48 operations which is the most that any group has. The translational symmetry of the unit cell was studied by Bravais in 1850 who showed that there are effectively only 14 different unit cells which can be used to describe each crystal lattice.

In order to complete the dynamical matrix it is in principle necessary to displace each atom in the primitive cell in each of the three directions. Since these calculations have to be done with large supercells they are expensive and time consuming. Fortunately, the number of displacements which need to be made can often be reduced significantly by using symmetry to
3.2. CALCULATING PHONONS FROM AB INITIO CALCULATIONS

determine which displacements are equivalent. In the case of highly symmetric structures such as the bcc structure, it may only be necessary to make one displacement. When calculating the dynamical matrix both the point-group symmetries [10] and the translational symmetries within the supercell may be exploited.

The application of symmetries is widely used in ab initio calculations as it can greatly reduce the computational effort required to calculate many properties of a crystal. For example, if two points in the Brillouin Zone are related by symmetry, the band structure at these points will be the same. It is therefore only necessary to calculate the band structure at one of these points. Similarly the charge density at these two points will be equal. The set of k-points used to sample the Brillouin zone in section 2.13.1 can be significantly reduced by determining which k-points are equivalent.

Symmetry elements may be described in terms of a $3 \times 3$ matrix $\tilde{S}$ which corresponds to either a rotation, reflection, or an inversion or it is simply the identity matrix, and a vector $v$ which is a translation by an amount other than a lattice vector. The matrix $\tilde{S}$ is an orthogonal matrix. This means that the inverse of $\tilde{S}$ is equal to the transpose ($\tilde{S}^{-1} = \tilde{S}^T$) and that $|\tilde{S}| = \pm 1$. Consider a symmetry element $\{\tilde{S}|v\}$ which maps atom $i$ to $I$ and atom $j$ to $J$. If atom $i$ is subject to a force $f_i$, atom $I$ is subject to a force $f_I = \tilde{S}f_i$. Displacing atom $j$ by $u_j$ is symmetrically equivalent to displacing atom $J$ by $\tilde{S}u_j$. According to equation 3.2, the force on atom $I$ due to moving atom $J$ is

$$f(I) = \Gamma(I, J) u(J). \quad (3.21)$$

Using the symmetry relations, this may be written as

$$\tilde{S}f(i) = \tilde{\Gamma}(I, J) \tilde{S}u(j). \quad (3.22)$$

Multiplying from the left by $\tilde{S}^T$ gives

$$f(i) = \tilde{S}^T \tilde{\Gamma}(I, J) \tilde{S}u(j) \quad (3.23)$$

but from equation 3.2 we know that $f(i) = \tilde{\Gamma}(i, j) u(j)$ therefore

$$\tilde{\Gamma}(i, j) = \tilde{S}^T \tilde{\Gamma}(i, J) \tilde{S} \quad (3.24)$$
or alternatively
\[ \tilde{\Gamma}(i, j) = \tilde{S} \tilde{\Gamma}(i, j) \tilde{S}^T. \] (3.25)

Using this relationship it is possible to calculate all the force constants using the minimum of computational effort.

### 3.2.3 Anharmonic effects

The calculations until now assume that the system is vibrating within the harmonic limit, or at least that the anharmonicity is negligible. If however, the displacement is too large or the harmonic contributions to the forces are zero due to symmetry then anharmonic terms have an effect. These terms are due to the third order derivatives of the energy. The force due to them however is proportional to the square of the displacements and is therefore independent of the direction in which the displacement is made. Consequently, these effects can be removed by averaging over pairs of displacements in opposite directions.

### 3.3 Reverse Engineering the matrix of force constants

Using the force constant matrix, it is possible to correctly calculate the vibrational frequencies at some special points in reciprocal space using *ab initio* calculations. The larger the number of primitive cells in the supercell, the larger the number of points at which we may calculate the vibrational frequencies. However, in order to produce a phonon density of states for example (see section 3.4), it is necessary to integrate the frequencies over the whole Brillouin zone. An infinitely large supercell is therefore required. If an atom in an infinite system is displaced a small amount however, only those atoms within a certain distance will feel any effect due to the displacement. The elements in the matrix of force constants corresponding to atoms at a greater distance will therefore be zero. Hence, if we use a supercell which is sufficiently large such that the forces are (effectively) zero on atoms at a distance of about half the size of the supercell away from the displaced atom, it is possible to construct a matrix of force constants for a pseudo-infinite supercell. It is then possible to calculate the vibrational frequencies at all points in the Brillouin zone.
3.3. REVERSE ENGINEERING THE MATRIX OF FORCE CONSTANTS

3.3.1 The pseudo-infinite matrix of force constants

The pseudo-infinite (PI) crystal is twice as big in each direction as the supercell used in the calculations. The atoms of the supercell are mapped onto those in the middle of the pseudo-infinite crystal; consider the position of the grey square within the black squares in the bottom diagrams of figure 3.1. To illustrate how the forces on the atoms in the pseudo-infinite crystal due to atomic displacements are evaluated, consider the displacement of the atom at the origin of the supercell (the star atom in the left half of figure 3.1). If atom x in the supercell is less than $\frac{1}{2}a_i$ away in each direction from the displaced atom, the force on it is given to the atom in the equivalent position in the pseudo-infinite crystal. However, if atom x is more than $\frac{1}{2}a_i$ in the $i^{th}$ direction, the force is assigned to the atom in the pseudo-infinite cell which is in the equivalent position but translated by $-a_i$. If the separation is exactly $\frac{1}{2}a_i$ away in the $i^{th}$ direction then the force on atom x is taken to be the sum of identical forces on two equivalent atoms, one at $-\frac{1}{2}a_i$ and the other at $\frac{1}{2}a_i$. Half of the force is therefore assigned to each of a pair of atoms in the pseudo-infinite cell: one in the equivalent position and one translated by $-a_i$ from that position. If it is exactly half a cell away in two or three directions then the force on atom x (in the supercell) is the sum of the forces felt by 4 or 8 equivalent atoms respectively. However, this division of forces should be a theoretical nicety, as the force components in the directions in which atom x is exactly half a cell away should be zero. If these components are not zero, the method of assigning forces to atoms in the pseudo-infinite cell, depending on where the atoms are in the supercell may produce incorrect results. All the forces on the atoms in the pseudo-infinite cell which are over half a cell away are taken to be zero. Figure 3.1 illustrates the procedure of mapping of atoms and the forces on them in the supercell, onto atoms and forces in the pseudo-infinite crystal. The forces due to displacing the other atoms in the pseudo-infinite cell may be found by symmetry. This method is sometimes referred to as the minimum image convention.
3.4 Dispersion Curves and Phonon Density of States

Having constructed the dynamical matrix and then the Fourier-reduced dynamical matrix, we may calculate the phonon dispersion curves and the phonon density of states. The phonon dispersion curves indicate how the vibrational frequencies depend on the wave vector of the mode. They are calculated by evaluating the Fourier-reduced dynamical matrix along lines of high symmetry and contain 3 distinct lines for each atom in the primitive cell. If a structure becomes dynamically unstable, vibrational frequencies along one or more of the branches will become imaginary. For simplicity, these are normally shown on the dispersion curves as being negative.

The phonon density of states is calculated like the phonon dispersion curves except that the Fourier-reduced dynamical matrices are diagonalised for all points within the first Brillouin zone to give the probability density function, $g(\omega)$, for the vibrational frequencies of the crystal.
3.4. DISPERSION CURVES AND PHONON DENSITY OF STATES

This is then normalised such that

\[ \int_{0}^{\infty} g(\omega) d\omega = 3n \]  

(3.26)

where \( n \) is the number of atoms in the primitive cell.

3.4.1 Brillouin Zone Sampling

The easiest way to produce a phonon density of states is to evaluate the Fourier-reduced dynamical matrix over a fine mesh of \( k \)-points and create a histogram of frequencies. While this method works reasonably well, the size of the bins must be a compromise between having bins which are small enough to capture the detail and yet big enough so that there are no anomalous empty bins. To overcome this, the variation of the frequencies between neighbouring points is calculated by interpolation. While ideally this would be done in all three dimensions, interpolating in only one direction is significantly simpler and results in significantly smoother density of states. It would also be possible to use the tetrahedron method as used to calculate the electron band structure [1].

If we use a linear interpolation scheme to help smooth our phonon density of states, the question arises of how much to add to each bin in the histogram. The total amount to add is the length of the line \( AB \). This is split amongst all the bins between the frequency at \( A \) and that at \( B \).

The amount to add to each bin is proportional to their widths and inversely proportional to the difference between the frequencies of the two points \( A \) and \( B \).

To illustrate this, consider a linear interpolation of frequency between two points \( A \) and \( B \) having frequencies \( f_A \) and \( f_B \) respectively, see figure 3.2. The vibrational frequency at a point \( p \in [A, B] \) is given by the straight line equation

\[ f(p) = (p - A) \frac{f_B - f_A}{B - A} + f_A . \]  

(3.27)

Given that the lower and upper bounds of a bin are \( f_1 \) and \( f_2 \) respectively and that the positions between where they occur are \( p_1 \) and \( p_2 \), the amount to add to this bin is equivalent to the distance between the points \( p_1 \) and \( p_2 \) and is given by:

\[ p_2 - p_1 = (f_2 - f_1) \frac{B - A}{f_B - f_A} = \delta \frac{B - A}{f_B - f_A} \]  

(3.28)
Figure 3.2: When interpolating the frequency between the k-points A and B the amount to add to the frequency bin \([f_1, f_2]\) is distance between the points \(p_1\) and \(p_2\).

where \(\delta = f_2 - f_1\) is the frequency width of the bin.

The set of k-points used is determined according to the Monkhorst Pack scheme [57], see section 2.13.1 [57] As a result there are no k-points on the boundaries and the interpolation scheme fails to fully sample the whole of the Brillouin zone. The solution is to create a new point outside the Brillouin zone. To do this we assume that the dispersion curve goes flat at the boundary and we can approximate it with a parabola fitted to the last and penultimate k-point. The extra point is the same distance from the boundary as the last real point but on the opposite side, and whose frequency is obtained by extrapolating the straight line between the last real frequency and the frequency at the boundary, as given by our parabola. The contribution to the phonon density of states is then determined as before using our real and pretend points but stopping at the boundary.

### 3.5 Thermodynamic contributions

For a complete description of the behaviour of a system it is necessary to determine its thermodynamic properties. These properties are dependent on the frequencies of the various modes of vibrations of the system and many may be calculated from the phonon frequencies calculated as in section 3.4. Arguably, the \textit{ab initio} calculations are done below zero kelvin since the calculated energy does not even include the zero point energy.
3.5. THERMODYNAMIC CONTRIBUTIONS

3.5.1 Helmholtz free energy

From statistical physics we know that the Helmholtz free energy per primitive cell is given by

$$f = -k_B T \ln z \quad (3.29)$$

where $k_B$ is Boltzmann’s constant, $T$ is the temperature. The partition function, $z$, is the usual sum of Boltzmann factors corresponding to all the possible energy levels of the system.

$$z = \sum_i e^{-\epsilon_i \beta} \quad (3.30)$$

where $\beta = 1/k_B T$.

If we assume that the particles (atoms or ions) behave like collections of independent oscillators which interact only weakly so as to reach thermodynamic equilibrium, we may determine the vibrational free energy by first calculating the energy due to one oscillator and then summing over the different oscillators. The eigenvalues for an oscillator of angular frequency $\omega_i$ are

$$\frac{1}{2} \hbar \omega_i, \frac{3}{2} \hbar \omega_i, \frac{5}{2} \hbar \omega_i, \ldots \quad (3.31)$$

and the partition function is

$$z_i = \sum_{s=0}^{\infty} e^{-\left(s+\frac{1}{2}\right)\hbar \omega_i \beta}$$

$$= e^{-\frac{1}{2} \hbar \omega_i \beta} \frac{1}{1 - e^{-\hbar \omega_i \beta}} = \frac{1}{2 \sinh \left(\frac{\hbar \omega_i}{2k_B T}\right)} \quad (3.32)$$

Putting this into equation 3.29 gives the vibrational energy of a single oscillator.

$$f_i = -k_B T \ln z_i = \frac{1}{2} \hbar \omega_i + k_B T \ln[1 - e^{-\hbar \omega_i \beta}] \quad (3.33)$$

For a crystal system with the set of vibrational frequencies $\{\omega_i\}$, the vibrational part of the free energy per particle is simply $\sum_i f_i$. The complete Helmholtz free energy also includes the static energy of the system, $u$. This is the energy which is calculated by the ab initio simulation programs. Therefore,

$$f = u + \sum_i \frac{1}{2} \hbar \omega_i + k_B T \sum_i \ln[1 - e^{-\hbar \omega_i \beta}] \quad (3.34)$$
In section 3.4 however, a frequency distribution function, as opposed to the discrete frequencies, was calculated. Consequently, the Helmholtz free energy per particle is written:

\[ f = u + \frac{1}{2} \int_0^\infty \hbar \omega g(\omega) d\omega + k_B T \int_0^\infty \ln[1 - e^{-\hbar \omega \beta}] g(\omega) d\omega . \]  \hspace{1cm} (3.35)

The second term is the quantum mechanical zero point energy. Although this is generally ignored in ab initio calculations it should be added if the true energy at zero kelvin is required. Having calculated the Helmholtz free energy it is possible using standard thermodynamic relations to calculate various other properties.

### 3.5.2 Entropy and energy

The entropy, \( s \), of the system at constant volume is

\[ s = -\left. \frac{\partial f}{\partial T} \right|_V = -k_B \int_0^\infty \ln[1 - e^{-\hbar \omega \beta}] g(\omega) d\omega + \frac{1}{T} \int_0^\infty \frac{\hbar \omega g(\omega)}{e^{\hbar \omega \beta} - 1} d\omega . \]  \hspace{1cm} (3.36)

Having now calculated the Helmholtz free energy and the entropy it is now possible to determine the internal energy of the system and from there the specific heat capacity. Substituting equations 3.35 and 3.36 into equation 3.29 gives the energy per primitive cell;

\[ e = u + \int_0^\infty \frac{1}{2} \hbar \omega g(\omega) d\omega + \int_0^\infty \frac{\hbar \omega g(\omega)}{e^{\hbar \omega \beta} - 1} d\omega . \]  \hspace{1cm} (3.37)

### 3.5.3 Specific heat capacity

The specific heat capacity at constant volume is the rate of absorption of energy and is obtained by differentiating the energy with respect to the temperature:

\[ C_V = \left( \frac{\partial e}{\partial T} \right)_V = k_B \int_0^\infty \frac{(\hbar \omega \beta)^2 g(\omega) e^{\hbar \omega \beta}}{(e^{\hbar \omega \beta} - 1)^2} d\omega . \]  \hspace{1cm} (3.38)

### 3.5.4 Equation of State

The equation of state links the pressure of a system to its temperature and volume. The pressure of a system at constant temperature is minus the derivative of the Helmholtz free energy with
3.6. IMAGINARY MODES

respect to volume

\[ p = -\left( \frac{\partial f}{\partial V} \right)_T. \]  

Substituting in equation 3.35 gives

\[ p = -\frac{\partial u}{\partial V} - \frac{1}{2} \int_0^\infty \hbar \omega \frac{\partial g(\omega)}{\partial V} d\omega - k_B T \int_0^\infty \ln[1 - e^{-\hbar \omega / \beta}] \frac{\partial g(\omega)}{\partial V} d\omega. \]

The first term, \(-\partial u/\partial V\), is usually known and in the case of \textit{ab initio} calculations is generally calculated by the simulation program. The dependence of \(g(\omega)\) on \(V\) however is more difficult to establish. One method is to calculate the force constants 3 times, once at \(V\) and then at \(\pm \Delta V\) and hence determine \(\partial g/\partial V\). This however requires 3 calculations for each point on the energy-volume curves. If the forces vary smoothly over a large range of volumes it may be possible to make one calculation at each point on the energy-volume curve and determine the forces at \(\pm \Delta V\) by interpolation. Whilst computationally more efficient this method would be messier to implement. A simpler solution would be to evaluate the Helmholtz free energy at a series of points throughout the pressure (volume) region of interest and determine an analytic form. The pressure of the system and hence the Gibbs free energy may then be simply evaluated from equation 3.39.

3.6 Imaginary modes

The methods outlined in the previous section break down when the dynamical matrix has negative eigenvalues which indicate that the structure is dynamically unstable. Normally, such structures are not seen experimentally. However, it is possible that the structure may be \textit{dynamically stabilised} at a sufficiently high temperature when its large entropy will cause it to have a lower free energy than the distorted structure. Unfortunately, the conventional quasi-harmonic approach developed so far produces energies which tend to infinity for such systems. An alternative treatment for imaginary (soft) modes must therefore be found.

The soft modes in such systems can be described using a Landau model, see section 4.5. In the Landau model, the unstable high-symmetry phase sits on the central maximum of a W shaped potential well while the stable distorted structures are found at the minima. An order
parameter $\xi$, is used to describe the amount of distortion in the system. Typically the double well is parametrised using a quartic polynomial $V(\xi) = A\xi^4 - B(T)\xi^2$. However, third order or higher terms imply the existence of phonon coupling which is assumed to be non-existent in the harmonic approximation. In the rhombohedral structure of Bi, section 4.5, the quartic polynomial fits the calculated variation of energy with $\xi$ between the minima very well. However, at larger values of $|\xi|$ the quartic term is too steep to provide an accurate model. Better fits to the well may of course be obtained with polynomials with higher order terms but these imply larger anharmonic contributions. Once the double well has been parametrised it is assumed that the energy contribution from it can be treated classically with energy of $k_B T$. The transition from the low symmetry distorted phase to the dynamically stabilised high symmetry phase occurs when there is sufficient energy to pass over the barrier in the middle of the well. The transition temperature is therefore the height of the barrier divided by Boltzmann’s constant. However, whilst this model can be used to produce pressure-temperature phase diagrams, the transition temperatures are not very reliable [5].

Recently however, Drummond and Ackland [3] have proposed a new model which is consistent with the harmonic approximation. Their new model describes the double well as an ordinary quadratic well plus a Gaussian bump:

$$V(\xi) = \frac{1}{2}m\omega_0^2\xi^2 + \epsilon \left( e^{-\xi^2/2\sigma^2} - 1 \right)$$

(3.41)

where $\epsilon$, $\sigma$ and $\omega_0$ are dependent on the wave vectors. An advantage of this form is that it can be used to model both the imaginary and real modes. In the later case $\epsilon$ is simply zero. A further advantage is that it is approximately quadratic in both the high and low energy limits. The harmonic frequency of a mode, which may be imaginary, about its centre is

$$\omega_c^2 = \omega_0^2 - \frac{\epsilon}{m\sigma^2}.$$  

(3.42)

The wave functions of the double well may be expressed simply in terms of the eigenfunctions of the simple harmonic oscillator. The energy eigenvalues can then be found by diagonalising a real symmetric matrix. The off-diagonal terms fall off rapidly as the energy is increased, so at large energies the system will behave as a simple harmonic oscillator which has well known eigenvalues. It is therefore only necessary to diagonalise the top left corner of the matrix to get
the first \( n_c + 1 \) energy levels. For \( n_c \) sufficiently large, the partition function may be written as

\[
Z = \sum_{n=0}^{n_c} e^{-\beta E_n} + \frac{e^{-\beta \hbar \omega_0 (n_c + 1)}}{e^{\beta \hbar \omega_0 / 2} - e^{-\beta \hbar \omega_0 / 2}}. \tag{3.43}
\]

The free energy is then

\[
f = -k_B T \log \left( Z \right), \tag{3.44}
\]

but there is no nice analytic form as in equation 3.33.

Before the free energy may be calculated, it is necessary to evaluate the parameters \( \epsilon, \sigma \) and \( \omega_0 \) which parametrise the well. To do this it is necessary to calculate the energy of the (primitive) cell with displacements corresponding to the wave vectors of all the high symmetry points in the Brillouin zone frozen into the crystal. If the energy of the undistorted structure is calculated then all three parameters may be evaluated by making distortions of only two different magnitudes along each of the wave vectors. The parameters may be determined elsewhere in the Brillouin zone by interpolation. The phonon density of states may then be calculated as described in section 3.4 except that fundamental frequencies \( \omega_0 \) need to be calculated from the frequencies obtained by diagonalising the dynamical matrix \( \omega_c \) using equation 3.42, and of course the free energy is evaluated from equations 3.43 and 3.44.

The temperature of the transition between the distorted low symmetry structure and the dynamically stabilised high symmetry structure is found in the usual way by comparing the Helmholtz or Gibbs free energies of the two structures. This also necessarily requires a separate calculation of the vibrational modes of the distorted structure.

### 3.7 Other Methods

In 1965 Sharma and Joshi proposed a method of calculating phonon dispersion curves from elastic constants \[78\]. Their method involves deriving expressions for the elastic constants in terms of the dynamical matrix. They then derived expressions for the dispersion curves along lines of high symmetry. Experimentally determined elastic constants were then used to generate their dispersion curves. In their original paper they use their method to calculate the dispersion curves of sodium. They find very good agreement with experimental results. In a
second paper they further validate their method by studying copper [79]. More recently the method has been used by Christensen and co-workers to study dispersion relations and phonon density of states in caesium and other metals [14]. In their work however, they calculated the appropriate elastic constants using \textit{ab initio} calculations to calculate the change in energy to small applied stresses, see section 7.7.

The methods of evaluating the dynamical matrix so far discussed have required making finite distortions to the system. The dynamical matrix can however also be evaluated analytically. This is relatively simple to do when analytic pair or many-body potentials are used to describe the interactions of the particles in a system []. However, recently it has been proposed that the dynamical matrix may also be calculated directly from \textit{ab initio} calculations using linear response theory. The ionic contributions can be calculated as for classic molecular dynamics from Ewald sums while the electronic contribution can be calculated via density functional perturbation theory [5]. The exchange and correlation energies are independent of that ionic positions and so to first order they make no contribution. This significantly simplifies the problem. The other main difference between this method and the finite displacement method discussed in the rest of this chapter is the size of the cell used in the calculations. In the latter method a small number of calculations are made using a large cell, whereas within the linear response method lots of calculations are required but on a small (primitive) cell. Within linear response theory the displacements of the periodic images of the atoms in the simulation cell may be modulated with a phase factor with arbitrary wave vector $q$. Thus phonon dispersion curves or densities of states can be evaluated by making separate calculations at each required $q$. As yet it is impossible to use linear response theory with ultra-soft potentials. However, CASTEP should soon be able to calculate phonon frequencies using linear response theory with norm-conserving pseudopotentials [91].

### 3.8 My work

As part of the work completed for this thesis, a computer program was written to calculate the phonon frequencies and eigenvectors at any set of given wave vectors and hence produce phonon dispersion relations and phonon densities of states. The program was based on one
written by Michele Warren [88] but was completely rewritten and included many more options and features. Unless otherwise stated everything detailed within this chapter, apart from the treatment of soft modes, has been implemented in the program. This section discusses the practicalities determining the dynamical matrix.

When calculating forces using *ab initio* codes, it is advisable to make the program symmetrise the forces. The system with a displaced atom will generally have a lower symmetry than the equilibrium structure. It is of course this reduced set of symmetry elements which should be applied. However, when the dynamical matrix is determined, the full set of symmetries of the equilibrium system plus the translations within the supercell should be applied.

Once a set of forces due to a displacement has been calculated, it is entered into the appropriate column of the dynamical matrix. Since the dynamical matrix is Hermitian, the forces are also entered into the corresponding row. As *ab initio* calculations are not exact, different calculations can erroneously give slightly different forces. Conflicts therefore occur as different calculations give different values for the same element of the dynamical matrix. If individual calculations are not sufficiently well converged, the set of forces from one calculation can also produce conflicting values when the point-group and translational symmetries are applied to the matrix. In the later case, the conflicts can occur since under the harmonic approximation displacing an atom forwards and backwards results in forces of the same magnitude. The calculated values, although possibly in good agreement will not in general be the same either because of anharmonic contributions or numerical errors. The numerical errors can be reduced by using a finer mesh for manipulating the charge densities. The first order anharmonic contributions can be removed by making two displacements in opposite directions, see section 3.2.3.

By applying extra symmetry elements to the forces, the harmonic approximation can be enforced and the numerical errors reduced. The required symmetry elements are those which map the displaced atom on to itself and which swap the sign of the displacement. This process ensures that the part of the dynamical matrix filled with the forces from one calculation, or pair of calculations, exhibits the correct symmetry. The conflicts arising due to using forces from several different calculations to fill the dynamical matrix can be reduced by creating a different dynamical matrix for each calculation. The various symmetry elements should be applied to each incomplete dynamical matrix. The value of an element in the final dynamical matrix is
then the mean value of the corresponding elements in the matrices from the individual calculations. If an element is not defined by a calculation then it is not included in the mean. Thus, if an element is determined by only one calculation, the mean value will simply be the value calculated.

The final condition which the dynamical matrix must satisfy is Newton’s third law which demands that there is no net force on a system due to the displacement of one of its constituent atoms. If this holds, the system will have three translational modes with exactly zero frequency. The forces produced by \textit{ab initio} calculations however only approximately satisfy this condition due to convergence and discretisation errors. Also, the charge density is interpolated on a discrete grid. If the lattice is displaced slightly, the positions of the ions with respect to this grid change slightly and the interpolation will produce slightly different results \cite{88}.

A comparison of the effects of symmetrising the forces and correcting for Newton’s third law is shown in figure 3.3. The main difference between the schemes occurs at the \textGamma point with the rest of the curves through the rest of the Brillouin zone being very similar. The phonon dispersion curves are for the bcc structure of barium. The sharpest cusps are obtained by enforcing the correct symmetry on the dynamical matrix. In order that the frequency at the \textGamma is zero, it is necessary to correct for the unbalanced forces or drift. Comparing the bottom left and the top right plots in figure 3.3 suggests that there is little anharmonic contribution to this system implying that the displacements are sufficiently small. However, averaging a pair of displacements without making any other correction does improve the results.
3.8. MY WORK

Figure 3.3: Comparison of different treatments of forces. The top left corner shows the full dispersion curves and the box indicates the region plotted in the remaining graphs. The letters indicate which combinations of modifications have been used: s for force symmetrisation; d for drift correction; and p for using a pair of calculations to correct for first order anharmonic contributions. spd therefore indicates that all 3 corrections have been applied. none indicates that no correction was applied.
Chapter 4

The Rhombohedral Structure

4.1 Introduction

At ambient pressure and temperature most elements have a close-packed structure such as face centred cubic (fcc) or hexagonal close packed (hcp). Most of the others have nearly close packed structures such as body centred cubic. A few have a relatively open structure, such as polonium which has a simple-cubic arrangement, but they are still highly symmetric. In this way semi-metals in group-V of the periodic table, arsenic (As), antimony (Sb) and bismuth (Bi) are all unusual as they all take a low symmetry rhombohedral structure.

4.2 The structure

The structure can be best visualised by imagining a simple-cubic structure since it is a special case of the rhombohedral structure. Instead of the usual cubic basis vectors consider three basis vectors which go diagonally across the faces of the cube (cubic (110), (101) and (011) directions) with an angle of 60° between them, similar to the primitive basis vectors of the fcc structure ((1/2 1/2 0), (1/2 0 1/2) and (0 1/2 1/2)). The unit cell now contains two atoms: one a quarter of the way along the diagonal and the other three quarters of the way along the diagonal. In the rhombohedral structures of As, Sb and Bi however the structure is stretched along the longest
Figure 4.1: The simple-cubic structure may be described by a rhombohedral cell containing 2 atoms with an angle of $\alpha = 60^\circ$ between the lattice vectors and with an internal parameter of $u = 0.25$ (left). The lower atom is at the centre of the cube. The right hand diagrams show the 110 planes of the simple-cubic structure (top right) and of the distorted rhombohedral structure (bottom right), both with the rhombohedral cells marked. The dash-dotted lines in all 3 diagrams indicate the $(1\ 1\ 1)$ direction.

The shape of the rhombohedral cell can also be described by the shear of the unit cell $\varepsilon$ or by the $c/a$ ratio of the unit cell [62]. All three methods also require the specification of either a length or the volume of the cell. In this work the rhombohedral angle is used since it may be simply specified in terms of the length of the basis vectors and the angle between them. This is the simplest description of the cell to visualise and requires no knowledge of coordinates used to describe the basis vectors. The description of the basis vectors are however not as neat as that when the cell is described by the $c/a$ ratio. More details of these two representations of the cell and their relationships to one another are given in appendix A.
4.3 Symmetry breaking

According to the theory of Jahn and Teller (section 2.13.3), if system with an odd number of electrons per atom has a high degree of symmetry and has degenerate energy bands, then the total energy may be lowered by distorting the structure. Similarly, the ground state energy of the group V elements may be lowered from that of the simple-cubic structure by stretching the unit cell along the (1 1 1) direction and moving the atoms within the unit cell closer together. This results in the atoms being reorganised in to planes two atoms thick, see figure 4.1. These distortions cause a loss of degeneracy in the bands near the Fermi level at the points Z and L compared with the simple-cubic structure. Figure 4.2 shows the band structure plots for the simple-cubic structure in bismuth as well as plots for the distorted rhombohedral structure at 3 different pressures: ambient pressure, 6 GPa and 11 GPa. To simplify the comparison between the band structures of the simple-cubic and rhombohedral structures, all calculations were made with the appropriate rhombohedral cell. In the simple-cubic, undistorted rhombohedral, structure the reciprocal lattice points Z and L are symmetrically equivalent. The point Z has coordinates $\left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right)$, L has $\left(0, \frac{1}{2}, 0\right)$, F has $\left(0, \frac{1}{2}, \frac{1}{2}\right)$ and Γ has $\left(0, 0, 0\right)$ with respect to the reciprocal lattice vectors of the rhombohedral cell [10]. As the pressure is increased the distortion decreases and the band gap closes up again.

The density of states of the rhombohedral structure, figure 4.3, shows that there is a dip at the Fermi energy corresponding to the pseudo band gap in the band structure which stabilises the distortion. The large peak centred on -10 eV in the density of states of the simple-cubic structure is also split by the distortion. This corresponds to the loss degeneracy of the two lowest energy bands in the band structure plots at the points Z and L. However, since both of the new peaks are below the Fermi energy this splitting does not affect the total energy of the system to the first order in the perturbation.

As the pressure is increased, the Pauli repulsion between neighbouring atoms increases, which in turn increases the energy of the distorted structure. The size of the distortion therefore decreases to minimise the increased effect of Pauli repulsion. As the distortion decreases, so does the band gap and hence the depth of the dip in the density of states at the Fermi energy. The net result is that the distortion decreases with pressure until, at sufficiently high pressure
the simple-cubic structure becomes stable (except that another phases intervenes).

![Graphs showing band structures](image)

**Figure 4.2:** Comparison between the band structures of the simple-cubic structure (top left) and the rhombohedral structure at different pressures: ambient pressure (top right), 6 Gpa (bottom left), and 11 Gpa (bottom right). In the band structure of the simple-cubic structure the points Z and L in reciprocal space are equivalent. However, this equivalence is lost when the cell is distorted to the ambient rhombohedral structure (top right). However, as the pressure is increased (bottom left then bottom right) the amount of distortion decreases and the band structure tends to that of simple-cubic. The splitting of the bands at the $\Gamma$ point also decreases with pressure.

### 4.4 Spin-Orbit coupling

The magnetic moment of an electron of angular momentum $\ell$ in orbit about an atom has two discrete components: $\mu_\ell$ is proportional to the angular momentum of the electron and $\mu_s$ is proportional to the spin $s$ of the electron [6]. Explicitly

$$\mu_\ell = -\frac{e}{2m_e} \ell$$  \hspace{1cm} (4.1)

$$\mu_s = -\frac{e}{m_e} s$$  \hspace{1cm} (4.2)
where $m_e$ is the mass of the electron. Classically when an electron moves with a velocity $v$ in an electric field $F(r)$, a magnetic field is induced

$$B = -\frac{1}{c^2} v \times r. \quad (4.3)$$

If the potential $V$ associated with the electric field is spherically symmetric we may write

$$F(r) = -\nabla V = -\frac{\partial V}{\partial r} r \quad (4.4)$$

which gives

$$B = \frac{v \times r}{rc^2} \frac{\partial V}{\partial r} = -\frac{\ell}{m_e rc^2} \frac{\partial V}{\partial r} \quad (4.5)$$

where $\ell$ is the angular momentum of the electron, $m_e r \times v$. The electron then interacts with this magnetic field since it has a magnetic moment $\mu_s$. The energy of this interaction is

$$W = -\frac{1}{2} \mu_s B$$

$$= -\frac{e}{2m_e^2 rc^2} \frac{\partial V}{\partial r} \ell \cdot s. \quad (4.6)$$

If the total angular momentum is $j = \ell + s$ then $j^2 = \ell^2 + s^2 + 2\ell \cdot s$ and we can write the interaction energy as

$$W = -\frac{e}{4m_e^2 rc^2} \frac{\partial V}{\partial r} (j^2 - \ell^2 - s^2). \quad (4.8)$$
CHAPTER 4. THE RHOMBOHEDRAL STRUCTURE

This classical equation may be transformed into a quantum mechanical expression by replacing the dynamical variables with their corresponding operators. The one electron Hamiltonian operator then becomes

\[ \hat{H} = \hat{H}_0 + \frac{\hat{L}^2}{4mr^2} f(r)(\hat{J}^2 - \hat{L}^2 - \hat{S}^2) \]  

(4.9)

where \( f(r) = -\frac{e^2}{4m_e r^2} \frac{\partial V}{\partial r} \) and \( \hat{H}_0 \) depends only on the radial coordinate \( r \). Since the operators \( \hat{J}, \hat{L} \) and \( \hat{S} \) are all independent of \( r \) and commute with each other, \( \hat{H} \) also commutes with each of them. The spin and angular-dependent parts of the energy are therefore eigenvalues of \( \hat{J}, \hat{L} \) and \( \hat{S} \). Normally the quantum numbers associated with the magnitudes of the total, angular and spin momenta are denoted \( j, \ell \) and \( s \). The total momentum \( j \) takes values in integer steps from \( |\ell - s| \) to \( \ell + s \) where \( \ell \) is an integer between 0 and the quantum number minus 1. The eigenvalue of \( \hat{J}^2 \) is \( j(j+1)\hbar^2 \) and those of \( \hat{L} \) and \( \hat{S} \) are similar. The contribution of the last term in equation 4.9 to the energy of the system is therefore

\[ E_{so} = \left\langle f(r) \right\rangle (j(j+1) - \ell(\ell+1) - s(s+1))\hbar^2 \]  

(4.10)

where \( \left\langle f(r) \right\rangle \) is the expectation value of \( f(r) \). The effect of spin-orbit coupling is therefore to remove the degeneracy of states with the same angular momentum \( \ell \) but different total momenta. If the angular momentum is zero then there is no splitting since the total momentum is equal to the spin momentum. If the angular momentum is non-zero then the energy of one member of the resulting doublet is raised by an amount proportional to \( \ell \) and the other is lowered by an amount proportional to \( \ell + 1 \). Figure 4.4 illustrates the effect of spin-orbit coupling: one band is lower and the other is raised, so to first order, there is no change in the total energy of the system. When crystal structures form, the potential \( V \) will cease to be spherically symmetric and \( \ell \) and \( j \) will cease to be good quantum numbers so the contribution of spin-orbit coupling to the total energy will be more complicated to compute. Qualitatively though the results are the same. A familiar example of spin-orbit coupling is the orange doublet in the emission spectrum of sodium.

In the heaviest group V element, bismuth, Gonze et al. [27] say that spin-orbit coupling is an important factor in the accurate determination of the density of states. The main effect on the band structure is to split the degeneracy of the d bands between \( \Gamma \) and L. This splits into
Figure 4.4: The effects of spin-orbit coupling on energy levels: one band goes up and the other goes down, so to first order there is no change in the total energy of the system.

two the peak in the density of states, which is just below the Fermi level. However, they also note that spin-orbit coupling has very little effect on the charge density. As the properties of a system depend only on the charge density in density functional theory, the effect of spin-orbit coupling should be negligible. Alas, neither VASP nor CASTEP support spin-orbit coupling so we were unable to test this hypothesis. However, for accurate determination of for example the optical properties, spin-orbit coupling will of course be important.

4.5 Landau Model

The internal parameter and the angle between the basis vectors of a rhombohedral cell are strongly connected and care has to be taken in setting up the system for ab initio calculations. If the initial configuration of the atoms in the cell corresponds to an internal parameter of 0.25, an extra symmetry element is created by the simulation programs which effectively prohibits the relaxation of the atomic positions. The simulation programs will therefore always incorrectly find the equilibrium structure to be simple cubic. Similarly if the basis vectors are not allowed to relax at the same time as the atomic positions, the programs will again find the

1According to the manual, the latest version of VASP does support it but unfortunately we were unable to obtain a copy as it has not yet been released.
wrong equilibrium structure. It is therefore necessary to start the simulations with an internal parameter not equal to 0.25 and to allow all degrees of freedom to relax simultaneously if the correct structure is to be found. In all cases the volume of the cell is kept constant to minimise the variation of the plane-wave cut-off energy, see section 2.14.2.

Since the internal parameter and the cell angle depend on each other then we may consider the energy landscape of the system as a function of only the internal parameter and the cell volume. The angle between the basis vectors at any particular point on this landscape is that which minimises the total energy. This landscape is symmetrical about \( u = 0.25 \): moving an atom along the \((1 \ 1 \ 1)\) direction towards its neighbour increases the separation between it and its neighbour on the opposite side by the same amount. Figure 4.5 shows a contour plot of the energy landscape of bismuth. The landscapes of arsenic and antimony are similar. The equilibrium rhombohedral structure sits in the bottom of the valley, whilst the simple-cubic structure sits in a meta-stable position on top of the ridge separating the two valleys. As the pressure is increased, the cell volume decreases, so the height difference between the valley bottom and the top of the ridge decreases as does the horizontal distance between the valleys.
Ultimately the ridge disappears and the two valleys merge. At this point, distortion becomes unfavourable and the equilibrium structure is simple cubic. In reality however, As, Bi and Sb have all transformed to a different structure before this pressure is reached. Figure 4.6 shows several slices of differing volumes through this landscape. Some of the cross sections intersect because the equilibrium volume of the simple-cubic structure is 70 Å³ which is smaller than that of the rhombohedral structure. Therefore, while the energy of the rhombohedral structure increases as the cell volume decreases, the energy of the simple-cubic structure actually decreases initially. This can be seen in figures 6.10 and 6.11. The double minimum form suggests the use of a Landau approach to describe how the distortion will behave with temperature. The free energy may be written in terms of the displacement of the atoms $\xi = 0.25 - u$:

$$G(\xi, V, T) = -A(T, V)\xi^2 + B(V)\xi^4 + E_0(V)$$  \hspace{1cm} (4.11)$$

where $E_0(V)$ is the energy of the simple-cubic structure. The cell angle for a particular value of $\xi$ is that which minimises the total energy, G. At zero temperature we may fit the parameters A and B to the difference in energy between the simple-cubic structure and the minimum energy of distorted rhombohedral structure $\Delta E$, and to the optimal distortion $\xi_0$. Although this is
quite a simple formulation it may be seen in figure 4.6 that for bismuth it fits the calculated values well between the minima $\pm \xi_0$. For displacements of the atoms greater than the optimal displacement however, the predicted energy increases much more quickly that the calculated values. Intuitively this should not matter too much since this part of the landscape will not be explored. At zero temperature the energy difference is

$$\Delta E(V) = \frac{A(0, V)}{4B(V)}$$

(4.12)

and the optimal distortion is given by

$$\xi_0(V) = \sqrt{\frac{A(0, V)}{2B(V)}}.$$  

(4.13)

Combining these two equations gives expressions for $A$ and $B$

$$A(0, V) = 2 \frac{\Delta E(V)}{\xi_0(V)^2}$$

(4.14)

$$B(V) = \frac{\Delta E(V)}{\xi_0(V)^4}.$$  

(4.15)

In the simplest, classical, picture we consider the mode to be an isolated oscillator with energy $k_B T$, in which case the barrier disappears when $k_B T = \Delta E$. We may therefore write the temperature dependence of the Landau parameter $A$:

$$A(T, V) = A(0, V) \left(1 - \frac{k_B T}{\Delta E}\right).$$

(4.16)

This model predicts that there will be a second order phase transition between the rhombohedral and the simple-cubic structures at a temperature of $T = \frac{\Delta E}{k_B}$. This transition may never be seen if this temperature is initially greater than the melting temperature of the elements, and if a different phase becomes stable before the phase transition temperature falls below the melting point.

### 4.6 Comparison with experiment

We have done ab initio calculations on the rhombohedral phases of bismuth, antimony and arsenic\(^2\). Details of the calculations are given in section 6.2. The calculated properties gener-

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\(^2\)Arsenic has been studied as a final year undergraduate project by Iain Roberts [74] partially under the supervision of the author. As a result, only a small amount of data on arsenic will be presented. However, the results presented although in agreement with the work of [74], are those of the present author.
#### 4.6. COMPARISON WITH EXPERIMENT

<table>
<thead>
<tr>
<th></th>
<th>calc. $V_0$ (Å$^3$)</th>
<th>exp. $V_0$ (Å$^3$)</th>
<th>% diff.</th>
<th>calc. $B_0$ (GPa)</th>
<th>exp. $B_0$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi</td>
<td>36.5</td>
<td>35.4</td>
<td>3.1</td>
<td>28.9</td>
<td>31</td>
</tr>
<tr>
<td>Sb</td>
<td>31.7</td>
<td>30.2</td>
<td>5.0</td>
<td>37.2</td>
<td>42</td>
</tr>
<tr>
<td>As</td>
<td>22.7</td>
<td>22.5</td>
<td>4.4</td>
<td>35</td>
<td>22</td>
</tr>
</tbody>
</table>

Table 4.1: Comparison between the calculated and experimental equilibrium volumes and bulk moduli for elements with the rhombohedral structure. The calculate data are determined by fitting the Birch-Murnaghan equation of state (section 2.14.6) to volume-energy data. Experimental bulk moduli are from WebElements [89].

...ally agree very well with those determined experimentally. The equilibrium volume per atom is in each case found to be greater than the experimental value by between 3 and 5 percent. The bulk moduli, which measure the curvature of the energy-volume curves, are also in reasonable agreement, see table 4.1 for details. More interesting is the comparison of the internal parameter $u$ and the cell angle $\alpha$. Unfortunately such data are more difficult to calculate experimentally than theoretically and in general there is little experimental data to compare with. Antimony is the exception as Schiferl et al. [75] have carefully collated results from earlier works and added further data under high pressures in a concerted effort to find a simple-cubic phase. They were unsuccessful in this respect. When comparing our calculations on antimony with experiment, the best agreement is obtained when the variation of the cell angle as a function of the internal parameter is considered, see figure 4.7. The equilibrium value for arsenic also lies nicely on our calculated curve. Our calculated values for bismuth, although still in good agreement with experiment are considerably lower than the limited experimental values. Since such good agreement is obtained with antimony and arsenic, this poorer agreement may suggest that the effects of spin-orbit coupling cannot be ignored. Unfortunately though, as previously mentioned, it was not possible to include spin-orbit coupling in our calculations. Studying graphs of the variation of cell angle and the internal parameter with pressure and volume, figure 4.9, suggests that in antimony and arsenic the experimental variations of both the cell angle and internal parameters are more accurately described as functions of pressure rather than of volume in our calculations. In bismuth however, the internal parameter is best described as a function of pressure whereas the cell angle is more closely related to the volume of the cell. This discrepancy may be down to the effect of spin-orbit coupling.
CHAPTER 4. THE RHOMBOHEDRAL STRUCTURE

Figure 4.7: Comparison of the calculated (triangles) and experimental (circles) variation of the angle with internal parameter in antimony and bismuth showing excellent agreement. Experimental values for antimony are from reference [75] and those for bismuth are from [19].

It can be seen in figure 4.8 that the \( u - \alpha \) curves for the three different elements lie on top of each other indicating that these properties are more of the rhombohedral structure and bonding than of the individual elements. The initial position on this curve is however governed by the element. Theoretical calculations have been done by several groups. Whilst the equilibrium structure reported by each group is the same, opinions differ over the possible existence of a rhombohedral to simple-cubic phase transition depending on the type of calculations employed. Mattheiss et al. [50] use an augmented plane-wave method to study arsenic. Using this method it is not possible to allow the shape of the simulation cell and atom positions to relax. Therefore they calculate the energy of the rhombohedral structure at different volumes with their initial internal parameter and cell angle. To determine the optimum values for \( u \) and \( \alpha \) at ambient conditions they calculate the energies for twenty systems covering all possible combinations: 4 different cell angles and 5 internal parameters. As the internal parameter and cell angle are not optimised at each different volume their energy-volume curve represents an upper bound on the energy of the rhombohedral structure. Mattheiss et al. note that it is not valid to make the common tangent construction on their energy-volume curves in order to calculate the transition pressure since they do all their calculations with the experimental optimum cell angle and internal parameter at ambient pressure. Instead they calculate the energy associated with
varying the internal parameter at different volumes. From this they estimate that the rhombohedral structure will transform smoothly to the simple-cubic structure at about \( V/V_0 = 0.8 \) or about 19 GPa. Experimentally Beister et al. find a transition at \( V/V_0 = 0.772 \) or 25±1 GPa. In the work of Needs et al. [62, 63] a plane-wave basis set is used and the internal parameter and cell angle are both allowed to relax. As here, Needs et al. find that as the pressure is increased so the rhombohedral structure tends towards simple cubic in agreement with the supposition of Mattheiss et al.. The energy of the simple-cubic structure is thus an upper bound on the energy of the rhombohedral structure. In Iain’s calculations the simple-cubic and rhombohedral curves merge with \( V/V_0 = 0.7 \) which compares favourably with the transition predicted theoretically by Chang et al. [13] at \( V/V_0 = 0.72 \). A first-order transition from rhombohedral to simple cubic at zero kelvin is therefore impossible. Continuous, second order transitions will however occur in all three elements at sufficiently high pressure. Experimentally these transitions will not be seen as other structures are stable at such high pressures.?? Experimentally, Beister et al. [8] report a rhombohedral to simple-cubic transition in arsenic which agrees well with that predicted by Mattheiss et al..

In antimony however both Iwasaki et al. [39] and Shiferl et al. [75] report not finding a rhom-
Figure 4.9: The variations of the internal parameter (left column) and cell angle (right column) in antimony (top row), arsenic (middle row) and bismuth (bottom row). In each graph the calculated values are plotted as functions of pressure (triangles) and volume (diamonds). The corresponding experimental values are also shown (circles and squares respectively). The filled circles show the variation of the internal parameter as a function of volume as predicted by Landau theory.
4.6. COMPARISON WITH EXPERIMENT

bohedral to simple-cubic transition. This is actually in agreement with our calculations since at the pressures where our calculated rhombohedral and simple-cubic energy-volume curves have merged, figure 6.11, antimony has transformed to the hotel phase. In our calculations, the energy difference between the rhombohedral and simple cubic structures at the experimental co-existence volume is only 1.5 meV, suggesting that the two phases are almost united. However, figure 4.9 shows that the calculated properties agree better with the experimental values if they are considered as functions of pressure rather than of volume. Experimentally, the transformation to the hotel phase occurs at around 85 GPa [75] which corresponds to a volume of between 27 and 27.5 Å³ per atom. At 27 Å³ per atom the calculated energy difference is almost 8 meV which is significantly greater than the errors in the calculations and therefore indicates that the two phases are still distinct. In disagreement with Iwasaki and Shiferl, Kabalkina et al. [43] reported a rhombohedral to simple-cubic phase transition. However, in private communication with Shiferl, Kabalkina pointed out that the transition only occurred in 6 out of 30 experiments and themselves suggested that the process is very sensitive to shear stresses. Since the calculated energy difference between these two structures is small, only a small shear force would be required to transform between them. If the experimentally applied pressure was not quite hydrostatic, it could provide the appropriate shear stress to induce a phase transition and hence explain Kabalkina et al.’s apparently anomalous results.

Such transitions could be caused by temperature dependent factors. As mentioned in section 4.5, the Landau model predicts a temperature dependent position for the rhombohedral to simple-cubic transition. Even so, this will not be a first-order transition. The pressure-temperature phase diagrams as predicted by the Landau model are shown in figure 4.10. The Landau model does not predict a simple-cubic phase for bismuth given that it melts at 544 K and transforms to monoclinic at 2.55 GPa, or 4 GPa according to our calculations, see section 6.2. At very high temperatures, antimony is predicted to have a simple-cubic structure even at ambient pressure. As the pressure is increased the transition temperature decreases. At 3.5 GPa the Landau model predicts the transition temperature to be about 300K. This pressure is based on the calculated pressure-volume relation at 0 K, the pressure at 300 K will therefore be higher due to thermal contributions. However, no such transition was seen by Iwasaki. Unfortunately, the internal parameter and cell angle predicted by the Landau model at room
temperature do not agree with the experimental values as well as those predicted by the basic ab initio calculations, see figure 4.9. A more detailed evaluation of the Landau model is currently impossible due to a lack of experimental data.

![Phase diagrams of antimony (left) and bismuth (right) as predicted by the Landau theory.](image)

Figure 4.10: Phase diagrams of antimony (left) and bismuth (right) as predicted by the Landau theory. To the left of the theoretical line is predicted to be simple cubic. The highest experimental points give the melting line.

Another prediction of the Landau model as developed here is a negative thermal expansion coefficient. Whilst this results in better agreement of the calculated and experimental equilibrium volumes, the experimental thermal expansion is positive. The Landau model gives a negative thermal expansion because it is incomplete. As developed above, the Landau model completely ignores the effects of the ordinary phonons with positive frequencies. To correct this, the energy contribution from these phonons needs to be calculated as usual, see section 3.5, and incorporated into a quasi-harmonic model.

The quasi-harmonic model of Drummond and Ackland (see section 3.6) also has the advantage of possibly producing a first-order transition. With the conventional Landau model, the phase transition is said to occur when the temperature is equal to the barrier height divided by Boltzmann’s constant, see section 4.5. Drummond and Ackland suggest however that the transition to simple cubic should occur when the Gibbs free energy of the dynamically stabilised simple-cubic structure as described by their quasi-harmonic model becomes lower than the Gibbs free energy of the rhombohedral structure.
4.7 Ab initio Molecular dynamics simulations

In order to investigate the effect of temperature on the bismuth rhombohedral structure we have done some molecular dynamics calculations, see section 2.14. Since molecular dynamics calculations are intrinsically very expensive only four systems have been studied. All four consist of a large rhombohedral cell containing nine small cells giving a total of 54 atoms. The total volume of the cell was 1877 Å³ so at 0 K the system pressure was about 1.8 GPa. The atoms were initially placed so that the system had an internal parameter of 0.23. The cell angle was fixed at 60° in two of the systems and at 56.65° in the remaining two. Unfortunately neither of the ab initio simulation programs available allow the relaxation of the cell during molecular dynamics runs. In order to determine the optimum cell angle it would therefore be necessary to do calculations in lots of cells with different angles.

As can be seen in figure 4.11, however, the size of the energy fluctuations in the systems make comparisons very difficult. In fact, the energies of the two systems at 300 K are so close that it is practically impossible to say which has the lower energy. Comparing the mean energy is also difficult since its value is dependent on which time interval the average is made. The differences are such that depending on the choice of time interval, either system can have a lower energy. The reason for the similarity of the energies can be found by comparing the

![Figure 4.11: Variation of energy as a function of time for all three systems.](image)
CHAPTER 4. THE RHOMBOHEDRAL STRUCTURE

radial distribution functions of the systems. The radial distribution functions give the number of neighbours that an atom has at each distance. The radial distribution functions shown in figure 4.12 were calculated over a period of 1 ps. The systems at 300 K and 150 K were allowed to evolve for 6.8 ps before the measurements were taken in order that they may reach equilibrium. The system at 500 K only equilibrated for 5 ps. A 1 fs time step was used in the simulations.

The distribution functions for both systems at 300 K have a double first peak. This indicates that the atoms within the supercells are displaced from the simple cubic equilibrium positions. That is, neither system has a simple cubic arrangement of the atoms. This similarity of the atomic arrangement explains why the two systems have such similar energy.

As well as showing the radial distribution, figure 4.12 also shows the cumulative distribution functions which show the total number of neighbours within a sphere of that radius. This serves as a useful check on the radial distribution function: the first (double) peak contains 6 atoms whilst the second contains 12. These are the numbers of first and second nearest neighbours in the simple-cubic structure. Figure 4.12 actually shows two types of radial distribution function. The dashed lines show the average of lots of radial distribution functions at different time steps and may be written as

$$\overline{R}(r) = \frac{1}{N_T} \sum_{t=1}^{N_T} \left\{ \sum_{i \neq j} \delta(r - |\mathbf{r}_i^t - \mathbf{r}_j^t|) \right\}$$  \hspace{1cm} (4.17)

where $N_T$ is the number of time steps and $\mathbf{r}_i^t$ is the position of atom $i$ at time $t$. The part within the curly brackets is the basic radial distribution function. The solid line is the radial distribution of the average positions of the atoms, that is

$$R_{\text{ave}}(r) = \sum_{i \neq j} \delta(r - |\mathbf{r}_i - \mathbf{r}_j|) \text{ where } \mathbf{r}_i = \frac{1}{N_T} \sum_{t=1}^{N_T} \mathbf{r}_i^t.$$  \hspace{1cm} (4.18)

In figure 4.12, the first peaks in all of the radial distribution functions are split. This indicates that in all cases the rhombohedral distortion is more stable than the undistorted simple-cubic structure. As the temperature increases, the peaks broaden and start to merge. However, there are still definitely two peaks in all cases.
The radial distribution functions also allow us to calculate the internal parameters. If the two first peaks are at $r_1$ and $r_2$ then the internal parameter is simply

$$u = \frac{r_1}{2(r_1 + r_2)}.$$  \hfill (4.19)

Identifying the position of the peaks however is not always easy. One way of locating the peaks is to fit a pair of Gaussians to the distribution function. Figure 4.12 gives an internal parameter of 0.240 at 300 K. This compares favourably with the value predicted by the Landau theory of 0.239 for a system with 35 Å$^3$ per atom. The molecular dynamics simulations were done with a volume of 34.75 Å$^3$ per atom. Given that the cell angle is 60°, it might be expected that there is perhaps a tendency to underestimate the internal parameter. This is further shown by the internal parameter of the distorted rhombohedral system which is 0.235. The internal parameter of the distorted cell at 150 K is slightly smaller (by $6 \times 10^{-5}$) than the same cell at 300 K. The simulation at 500 K was done using the undistorted cell and its internal parameter is 0.241 which is larger than found in the same cell at 300 K.

Initially the first and third systems had temperatures of 300 K and the second 500 K. The tem-
temperature throughout the simulation period was controlled by a Nosé thermostat, section 2.14. Figure 4.13 shows the evolution of the temperature in the systems with time. It can be seen that the temperature fluctuates by less than about 3% in the two simple-cubic systems. The fluctuations in the rhombohedral system are however larger but are still less than 10%.

The temperature and energy of the system initially at 150 K evolve nicely for the first 5500 time-steps. The system then apparently goes haywire, figure 4.14. It has undergone a phase transition. The induced large fluctuations in temperature and in energy are due to the small system size. In a larger (real) system, the latent energy of the transition would be dissipated throughout the crystal.

Some information about the nature of the transition can be gleamed by studying the radial distribution functions before and after the event, figure 4.15. Before the transition, the second peak in the mean radial distribution function is single and although the second peak in the radial distribution function of the average positions is split at the top, it is joined at the bottom. After the transition pressure however, the top of the second peak in the mean radial distribution function has split and the second peak in the radial distribution function of the average positions is completely split. Closer inspection also shows that the splitting of the first peak, in both types of distribution function has increased. It therefore appears that the system has initially
tended towards being more simple cubic. Full transition does not occur since the cell angle is fixed at 56.65°. However, there is then a first-order phase change and the system becomes definitely rhombohedral in nature. The radial distribution of the initial (distorted) rhombohedral arrangement is also shown for comparison. The radial distribution function after the transition is significantly closer to the initial distribution function than the one just before the transition.

More information can be obtained by studying the change in the local neighbourhood of the atom at the centre of the supercell. An initial study suggests that the phase transition is a disorder → order transition: Before the transition, there is a much larger spread in the separations of the atoms in the (111) planes and the separations of atoms in neighbouring (111) planes than there is afterwards. In the perfect simple-cubic structure these should all be identical. These separations are generally between about 4.2 Å and 5 Å and so these neighbours are responsible for the second major peak in the radial distribution function. While the splitting of the first peak is primarily due to the displacement of the atoms within the (rhombohedral) primitive cell, the splitting of the second major peak is due to the distortion of the cell. This explains why the second peak in the system, with a cell angle of 60° and originally at 300 K is so much...
Figure 4.15: Radial distribution functions for the 150 K system in its initial configuration (top), before (bottom left) and after (bottom right) the phase transition. The solid line is the RDF of the mean atomic positions and the dashed line is the mean RDF.

The system at 500 K evolved for almost 2 ps less than the other systems.

4.8 Phonons

Another way to consider the rhombohedral distortion is in terms of phonons. We have calculated the phonon dispersion curves and the phonon density of states for the rhombohedral structure in bismuth. The calculations were done using a simple-cubic supercell containing 64 atoms. The dynamical matrix was determined by calculating the forces due to displacing the
first atom in both the positive and negative x-directions. In both cases the magnitude of the displacement was 0.0004 times the primitive lattice parameter. The structure is clearly unstable with respect to vibrational modes with wave vectors of \( \frac{1}{2} \frac{1}{2} \frac{1}{2} \), the R point phonon mode. This corresponds to a displacement of the atoms in the (111) direction such that atoms get alternately closer to and further away from each other.

The phonon density of states was produced by integrating over all the possible wave vectors in the Brillouin zone using an 80\(^3\) mesh. This could be used to calculate the Helmholtz free energy according to Drummond and Ackland’s scheme for treating imaginary modes, section 3.6. If the phonon density of states for the rhombohedral structure was also calculated, a search for a rhombohedral to simple cubic transition at high temperatures could begin.

4.9 Summary

In this chapter we have done ab initio calculations of rhombohedral structures in bismuth and antimony. The simple-cubic structure is a special case of the rhombohedral structure. As the pressure is increased, the distortion decreases towards simple cubic. At 0K, there is a continuous first-order transition from rhombohedral to simple cubic. However, in bismuth a
transformation to a monoclinic phase happens first. The increase in the rhombohedral angle towards 60° and the reduction in the displacement of the atoms from the simple cubic sites, with increasing pressure, is in good agreement with that seen experimentally. We find that at 0K it is not possible to have a first-order transition. The simple Landau model proposed also precludes a first-order transition at finite temperature. As the temperature is increased, the Landau model predicts that the rhombohedral structure will tend towards simple cubic, with a first-order transition at sufficiently high temperature. However, there is no experimental data available to confirm or disprove this suggestion. The downside is that it leads to worse agreement between the calculated distortion and that measured experimentally, when compared at equal temperatures. This leads to the prediction that antimony should be simple cubic at 300K, just before the transition to the next phase. However this is not what is seen experimentally by Iwasaki et al.. A better approach would be to use the quasi-harmonic method of Drummond and Ackland to calculate the Gibbs free energy of the simple-cubic structure and to compare this with the Gibbs free energy of the rhombohedral structure. This could lead to a first-order transition. However, it requires calculations of the phonon density of states for both the simple-cubic and the distorted rhombohedral structure at many different pressures, which will be time consuming to perform.

Using ab initio molecular dynamics, it is possible to study systems at finite temperature. We
have done such calculations in an attempt to verify the existence of a rhombohedral to simple-
cubic transition at high temperature. The results presented do suggest that the amount of dis-
tortion does decrease with temperature. However, the occurrence of a phase transition in the
system at the lowest temperature leads us to wonder if, at a later time, the other systems will
also undergo a similar phase change. Further work is required to give a more definitive answer.
Chapter 5

The Hotel Structure

The structure of the fourth phase of barium (Ba IV) has survived until recently without a satisfactory description. Previous X-ray diffraction studies \[45, 92\] assigned to it a tetragonal structure or monoclinic. However, these solutions often did not account for some of the minor peaks on the diffraction patterns but instead put them down to impurities in the sample, or remnants of another phase.

In 1997 Nelmes \emph{et al.} carried out a new study. By increasing and decreasing the pressure several times they succeeded in growing a single crystal of the allusive phase. Unusually, the X-ray diffraction pattern had not only bright Bragg peaks characteristic of a nicely ordered crystal but also lines of diffuse scattering indicative of disorder in the sample.

After scratching their heads for a while they realized that the juxtaposition of Bragg peaks and diffuse lines was also seen in the diffraction pattern of \(\alpha,\omega\)-dibromoalkane / urea inclusion compounds \[31\]. In these organic compounds, urea \((CO(NH_2)_2\) forms a honeycomb structure with linear channels parallel to the normal of the plane of hexagons. This is known as the host structure. These channels are filled with \(\alpha,\omega\)-dibromoalkane \((Br(CH_2)_nBr; n = 7 - 10)\) forming a guest structure. As the host and guest structure do not have the same periodicity along the channel axis, they are described as being incommensurate. The linear-mercury-chain compound \(Hg_{3-\delta}AsF_6\) also forms a host-guest type structure. The host lattice comprises a tetrahedral arrangement of the arsenic and fluorine atoms. The mercury ions form guest chains.
which are incommensurate with the host lattice [32, 33]. These compounds have several interesting properties such as anisotropic electrical conductivity.

Nelmes et al. have shown [64] that Ba IV consists of two interpenetrating but incommensurate structures. The barium host comprises stacked pairs of squares of atoms but with consecutive layers rotated through forty-five degrees. Viewed along the $c$ axis, the atoms are arranged in octagons with consecutive atoms alternating between two levels. The guest atoms form chains through the centre of these rings, see figure 5.1. The host and guest structures are necessarily commensurate in the $a$ and $b$ directions but are incommensurate along $c$.

![Figure 5.1: Schematic representation of the Ba IV structure. The host atoms (dark symbols) with chains of guest atoms (light symbols) are projected onto the ab plane. The host atoms are labelled with their z coordinates. The arrows labelled $a_s$ and $b_s$ are projections of the supercell vectors used in the calculations.](image)

Suggesting that a pure element may adopt a structure which contains effectively two different types of atom may initially seem fanciful. However, about the same time, and completely independently, Schwarz et al. proposed a similar structure for the fourth phase in rubidium[77]. The only significant difference being that Schwarz et al. said that their host and guest structures were commensurate.

The structure is further complicated by the appearance of three possible arrangements of the guest atoms. Nelmes et al. report seeing a disordered arrangement with a tetragonal unit cell and an ordered arrangement which can be described by a monoclinic unit cell. At higher pressure, another arrangement with an orthorhombic unit cell appears.
5.1 Setting up the simulations

Simulation of the hotel structure poses new problems: to properly describe the structure we need two independent unit cells which are incommensurate in one direction. However, all the simulation programs apply periodic boundary conditions and only allow the specification of one cell. Therefore we approximated with a similar commensurate structure: the pseudo Ba hotel. The pseudo Ba hotel structure has two variations, of which both have a monoclinic supercell (labelled s). The original version contains 8 host atoms and 3 guest atoms while the larger version contains twenty host and seven guest atoms. In the smaller cell, the ratio \( c_{\text{host}}/c_{\text{guest}} \) is 1.5 whereas the same ratio in the 27 atom cell is 1.4 which is significantly closer to the experimental ratio of 1.39. In both cases the two short basis vectors are \( a_s = \frac{1}{2}(b_{\text{host}} + a_{\text{host}}) + \frac{1}{2}c_{\text{host}} \) and \( a_s = \frac{1}{2}(b_{\text{host}} - a_{\text{host}}) + \frac{1}{2}c_{\text{host}} \). The long vectors are \( 2c_{\text{host}} \) and \( 5c_{\text{host}} \) for the small and large supercells respectively. These vectors were chosen so that the host structure is built correctly. The host cell has dimensions \( a_{\text{host}} = b_{\text{host}} = 8.42 \) and \( c_{\text{host}} = 4.74 \) Å at 12.1 GPa. Experimentally, the guests can be found in one of three arrangements each requiring a slightly different cell. One of the cells is partially disordered with the same a and b basis vectors as the host but with \( c_{\text{guest}} = 3.41 \) Å. On ordering, the guest structure can undergo a monoclinic distortion to one of four similar cells. One of these cells has \( a_{\text{guest}} = 8.46 \) Å, \( b_{\text{guest}} = b_{\text{host}} \), \( c_{\text{guest}} = 3.43 \) Å and \( \beta = 96.15^\circ \). The others are related to this one by \( 90^\circ \) rotations about the c axis. This corresponds to a displacement of atoms in the nearest neighbouring chains by 0.48 Å. The nearest neighbouring columns are those at \( 45^\circ \) to each other in figure 5.1.

Since our supercell itself is monoclinic, so is the arrangement of guest columns within. In the pseudo Ba hotel however, the monoclinic angle of the guest cell is fixed by, although not the same as, the monoclinic angle of the supercell used to describe the host cell. The guest monoclinic angle is not necessarily the same as that of the host structure because the basis
vector can be chosen so that it goes to any of the atoms in the neighbouring column. Since the positions of the guest atoms are fixed by the cell of the host structure, so the monoclinic angle of the guest structure is confined to be one of only a few discrete values. Since all the guest atoms are equivalent, (nominally at least), the guest monoclinic angle is the smallest member of the set defined by the host structure. In the pseudo Ba hotel, the relative displacement of the neighbouring columns is the difference between the guest separation $\frac{1}{2} c_{\text{host}}$. In the smaller cell, the guest separation is $\frac{2}{7} c_{\text{host}}$, hence the relative displacement of the guest columns is $\frac{1}{6} c_{\text{host}}$. In contrast, the guest separation in the larger pseudo Ba hotel is $\frac{5}{14} c_{\text{host}}$. Hence the neighbouring guest columns are displaced relatively to each other by $\frac{3}{14} c_{\text{host}}$. These displacements give guest monoclinic angles of $97.6^\circ$ and $99.7^\circ$ respectively. Unfortunately, these angles are not in such good agreement with the experimentally observed value as first appears. The reason is that the experimental guest cell is a base-centred monoclinic cell whereas the guest cell in the pseudo Ba hotel is a primitive monoclinic cell. The corresponding angles for the pseudo Ba hotel base-centred monoclinic cell are $100.6^\circ$ and $113.6^\circ$ for the small and large supercells respectively.

Another difference between the real and pseudo Ba hotel structures, which has already been mentioned, is the ratio $c_{\text{host}}/c_{\text{guest}}$. We can consider the pseudo Ba hotel as being the real structure with extra guests pushed in. As a result we can attempt to provide a correction for the elastic energy gained by squeezing in the extra guest atoms. The elastic energy may be estimated by stretching (straining) the supercell along the c-axis and measuring the resulting stress. The corresponding elastic constant $c_{33}$ is simply stress/strain.

An alternative method is to calculate the change in energy due to the applied strain. This can then be related to the elastic constant through equation \( \Delta E = V/2 \cdot c_{33} e^2 - 2 PV e \) (5.1)

where $e$ is the magnitude of the strain applied. The first order change due to not being at atmospheric pressure may be removed by averaging over the positive and negative strains. Finally,

\[ c_{33} = \frac{E_+ + E_- - 2E_0}{Ve^2} \] (5.2)
where $E_+$ and $E_-$ are the energies of the strained crystal and $E_0$ is the energy of the unstrained crystal. $V$ is the volume of the unstrained crystal.

If we assume the host and the guest structures independently to have the same elastic constant $c_{33}$, the change in energy due to forcing the guest atoms into the host structure is

$$\Delta E = \frac{V}{2} c_{33} \left[ 1 - \frac{\gamma_{\text{exp}}}{\gamma_{\text{calc}}} \right]^2$$  \hspace{1cm} (5.3)

where $\gamma$ is the ratio of $c_{\text{host}}/c_{\text{guest}}$.

For the 11 atom cell with a volume of 34.45 we find $c_{33}=0.483$ or 0.5 eVÅ$^{-3}$ which is 77.3 or 80 GPa. This leads to an elastic energy of 0.045 eV (0.05 eV). For the 27 atom cell we find $c_{33}=0.692$ eVÅ$^{-3}$ or 110 GPa at 33.73 Å$^3$/atom. This corresponds to an elastic energy of $6 \times 10^{-4}$ eV/atom. By including the elastic correction, the hotel phase as described by the 11 atom cell becomes the stable phase between 10 GPa and 21 GPa. Clearly, the exact transformation pressures are sensitive to this correction. This stability can be seen most easily by considering the difference in the enthalpies of the different structures. See inset graph in figure 6.7.

The hotel structure in bismuth has a different arrangement of the guest columns to that found in barium. In bismuth, there is only one arrangement of guests as opposed to three in barium. The guest atoms in bismuth can be described using a body-centred tetragonal cell as opposed to the base-centred monoclinic cell used in barium. Although the bismuth host structure has the same atomic arrangement as barium’s, the bismuth cell is squatter. That is

$$\frac{a_{\text{host}}}{c_{\text{host}}} |_{\text{bismuth}} > \frac{a_{\text{host}}}{c_{\text{host}}} |_{\text{barium}} .$$  \hspace{1cm} (5.4)

As a result the ratio $c_{\text{host}}/c_{\text{guest}}$ in bismuth is only 1.31. So that our pseudo Bi hotel was as close to the real structure as possible, a tetragonal supercell was used. The lattice vectors were simply $a_s = a_h$, $b_s = b_h$ and $c_s = 3c_{\text{host}}$. Two columns, each of four atoms were squeezed into the host structure: One down the z-axis and one through the centre of the cell. The column in the centre was displaced upwards by half the guest-guest distance with respect to the column along the z-axis so as to capture the body-centred nature of the guest structure. The ratio $c_{\text{host}}/c_{\text{guest}}$ in our pseudo Bi hotel was $\frac{4}{3}$ which is close to the 1.31 seen experimentally. As a result, our calculations predicted the pseudo Bi hotel to be stable without any need for elastic...
energy corrections. Given the proximity to the experimental ratio, such corrections would be very small. The reciprocal space of the 11 atom pseudo Ba hotel was sampled using a 3x3x4 Monkhorst-Pack k-point set giving 12 irreducible k-points. The accuracy of this mesh was tested by checking the effect of increasing mesh size in each direction in turn. Increasing the mesh size in the c-direction to 5/6 changed the energy by 0.1 meV whereas changing the mesh size in the other direction to 4/5 changed the energy by 0.1 meV.

The calculations on the 27 atom cell were done with a 2x2x4 k-point mesh. This was unfortunately insufficient to produce as accurate energies, but the calculations with finer meshes were too large for the system to relax, even on the parallel computers. Although the results obtained with the large cell provided a useful insight into the interactions of the host and guest atoms and a useful verification of the elastic correction to the 11 atom cell, they have not been used in the study of the complete phase behaviour of barium. The calculations on pseudo Bi hotel were done using a 4x4x6 mesh, giving 9 irreducible k-points. The resulting energies were converged to within 1 meV.

5.2 Zero frequency phonon mode

In order to calculate the properties of the hotel structure it is necessary to make a decision about the vertical position of the columns of guest atoms. As $c_{\text{host}}/c_{\text{guest}}$ is irrational, the choice is arbitrary since a different choice simply corresponds to examining a different part of the real structure. It follows therefore that the energy of the structure should be independent of the vertical position of the column of guest atoms. This property of the hotel structure was used to check the validity of our relatively small supercells. As table 5.1 shows, the calculated energy is independent of the position of the guest column. The differences in energy are comparable to the accuracy in terms of k-point convergence of the calculations. Each time the guest column was displaced vertically the whole system was allowed to relax again. This is correct since the specific location of the guest atoms within the column may perturb the host structure. On each occasion however, there was only small variations in the positions of the atoms. We therefore claim that although the supercell is a commensurate approximation to the hotel structure it gives accurate answers.
5.2. ZERO FREQUENCY PHONON MODE

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</tr>
<tr>
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<td>-1.126</td>
</tr>
<tr>
<td>0.49</td>
<td>-1.125</td>
</tr>
<tr>
<td>0.735</td>
<td>-1.124</td>
</tr>
</tbody>
</table>

Table 5.1: Variation of energy due to shifting the column of guest atoms up with respect to the host structure in the 27 atom cell. The offset is compared to the vertical separation of the guest atoms.

Displacing the guest columns neither increases nor decreases the energy of the system. This displacement therefore corresponds to a zero frequency phonon mode, or phason. In practice although the final energy may be the same there may however be a small barrier due to the local rearrangement of the atoms preventing the guest column sliding.

We have also performed similar calculations for the bismuth hotel structure. Both guest columns were moved up equally so preserving the relative offset of the guest positions. We found that the energy change due to shifting both guest columns by 0.32 of the guest-guest separation is smaller than the accuracy of the calculations. The calculations were done with a system volume of 29.4 Å³/atom. The pseudo Bi hotel is therefore an excellent description of the real structure.

Another vibrational mode which could occur in the guest structure is the displacement of neighbouring guest columns with respect to each other. The pseudo Bi hotel would lend itself very well to this type of investigation since it has two independent columns. Also, although the guest separation is slightly smaller than that observed experimentally, the pseudo Bi hotel is very close to the real structure. Calculations were attempted with the guest column along the z-axis starting at 0.32 of the guest separation and the other column starting at 0.14 of the guest separation. After one relaxation, the energy seemed to be the same as in the other calculations. However we were unable to verify this properly due to the unreliability/temperamental nature of the sun parallel computer in Edinburgh. Attempts to do something similar with the pseudo Ba hotel failed for the same reason.
5.3 Guest separation

Initially, the guest atoms were distributed evenly in their columns. During the calculations, their positions were allowed to relax without any artificial constraints. In the pseudo Bi hotel, the guests were found to move so as to also form dimers. At 1.0 GPa each atom moved by almost 6.5%. This results in a 13% change in guest separation. The centre guest column was initially displaced by $\frac{1}{2}c_{\text{guest}}$ with respect to the column along the z-axis. The dimerisation was the same in both columns. However, there was a net lowering of the centre column, giving a total relative displacement of 0.61 of the guest separation.

At higher pressures, the magnitude of the dimerisation is reduced. At 8.6 GPa the separations change by only 7.5%. The guest column in the centre has again lowered with respect to the guests along the z-axis. However, the total displacement was only 0.58 of the guest separation. This corresponds to approximately a 3% reduction in the lowering due to the increased pressure. Displacing both columns vertically by 0.32 and 0.64 of the initial guest separation made no difference to this dimerisation.

In the 11 atom pseudo Ba hotel there was also some displacement of the guest atoms. The middle and top guest atoms got 2.7% closer while the separations of the bottom and middle atoms and of the bottom and top atoms increased by almost 1.4%. In the 27 atom pseudo Ba hotel, some of the guest atoms got closer and others separate. However, the magnitudes of the changes in the displacements of the guest atoms were less than 0.5%. Also, although the changes in the separations tended to alternate between increasing and decreasing, the magnitudes of the variations were not equal.

We suggest therefore that the dimerisation of the guest atoms is an artefact of the commensurate nature of the pseudo hotel structures, which diminishes as the ratio $c_{\text{host}}/c_{\text{guest}}$ of the pseudo hotel structure tends towards the irrational experimental value.
5.4 Electron type

The study of the electronic character in the hotel structure, as is any other complex structure, is inherently difficult since there is no unambiguous way of assigning electrons to atoms, see section 2.14.3. The task is made more difficult in the hotel structure since some of the guest-host separations are unusually small. If the Wigner-Seitz radius is chosen, as suggested, so that the total volume of the spheres is equal to the volume of the supercell then there will be some double counting of electrons. If however, the radius is chosen to be less, then there will be some electrons or “parts” of electrons which are not counted at all. Even if the Wigner-Seitz radius is chosen so that the volumes agree, there will be some regions of plane waves which will not be projected on to the spherical harmonics of an atom and there will also be some regions which will be projected on to two or more sets of orbitals.

Despite the difficulties we will attempt to say something qualitative about the electron character in the hotel structures. In the barium hotel the Wigner-Seitz radius was chosen to be 2.004 Å, giving a total volume equal to that of the supercell. The volume of the supercell corresponded to the system being at a pressure of about 13 GPa. In an attempt to reduce the errors due to the guest atoms being too close to the host atoms, the average occupancy of each atom was calculated using the projections from the four simulations with the guest column at different heights. In all calculations only 201 electrons were accounted for instead of 216. This figure does not however account for those electrons which have been counted more than once. The number of missing electrons is therefore greater than 15.

Figure 5.2-top shows the number and type of electrons on each atom. It appears that the guest atoms have more electrons than do the host atoms. This could be that the host atoms donate electrons to the guest columns or it could also be an artefact of the infamous double counting. The difference in the electron type is however more convincing. Figure 5.2-top suggests that the electrons on the guest atoms have more d-type character and less s-type character than the electrons of the host atoms. The differences in the number of p-type electrons are significantly smaller but the graphs suggest that the guest atoms have slightly more p-type electrons than do the host atoms. This is however contradicted by figure 5.2-bottom which shows the proportion of each type of electron on each atom. In agreement with figure 5.2-top however the host
atoms have less s-type electrons and more d-type electrons. Although care has to be taken in the interpretation of these results, it is probably possible to say that the reduction in the number of s-type electrons and the increase in d-type electrons of the host atoms compared to the guest atoms is real. This claim may be supported by considering the nature of the s- and d-type electrons. The s-type electrons are in 6s orbitals and are therefore relatively loosely bound and so these are the most likely electrons to be counted more than once. This would suggest that the guest atoms should have more s-type electrons that the host atoms. Conversely the 5d electrons are more tightly bound suggesting that they are less likely to be counted more than once which suggests that the guest atoms should have the same number of d-type electrons as the host atoms. Having said all of the above, figure 5.2 also shows that any effect is very small. Given the smallness of the effect and the fact that many electrons remain unaccounted for, it seems impossible to say that there is any significant charge transfer between the host and guest structures. There may be some charge transfer, and there may be differing quantities of each type of electron on the host and guest atoms, but more accurate measurement techniques are required. Since barium is a metal, there could well also be some delocalised electrons not belonging to either group in particular. A similar study of the charge in the pseudo Bi hotel was carried out but produced similarly empty results.

A more productive comparison is that between the average number of each type of electron on an atom in the pseudo Ba hotel and on an atom in the hcp structure. As can be seen in figure 6.4, there is excellent agreement between the quantities of each type of electron in each structure. This explains why the analytic screened electrostatic potentials of Hafner and Heine discussed in section 6.1.3 appears to provide as good a description of the hotel phase as it does of the hcp phase (see figure 6.6).

The pseudo bismuth hotel has about 0.3 6d electrons and only 2.7p electrons. This corresponds to the transfer of 0.3 electrons from p-type orbitals to d-type compared with the electron configuration of the ambient phase.
5.4. ELECTRON TYPE

Figure 5.2: Projections of electron type in the barium hotel at about 13 GPa (top) suggest that the guests have fewer s-type electrons and more d-type electrons than do the guests. The proportion of each electron type (bottom) . Please write some more. See text.
5.5 Comparison between the hotel and hcp structures

The similarities between the hotel and hcp structures do not stop at having the same quantities of each type of electron. The dramatic decrease in the hcp ratio $c/a$ causes the shell of nearest neighbours to be split in two. The splitting results in two preferred distances for the atoms that would otherwise all be in the nearest neighbour shell. Analysis of the separations within the host structure of the hotel also crudely shows two preferred separations.

![Figure 5.3: Comparison of the bond lengths in hcp and the barium hotel structure. The nearest neighbour distance in the bcc structure is also shown.](image)

This similarity between the bond lengths suggests that the hotel structure represents another way of arranging the atoms such that they lie as close to the minima of the screened electrostatic potential as possible.

An alternative view of the nearly free electron picture [42] is that the energy is lowered by the perturbation of the states near the Fermi surface; this favours structures which have Brillouin zone faces close to the Fermi vector. The incommensurate barium hotel has two Brillouin zones, one for the host and the other for the guest structure. The (221) facet of the host Brillouin zone, the (111) facet of the guest Brillouin zone and the (220) facets of both are all close to the divalent free-electron Fermi vector [20].
5.6 Summary

We have successfully completed the first *ab initio* calculations on the newly identified hotel structures. Since the host and guest parts of the hotel are incommensurate, it was not possible to model the exact structures. Instead we created pseudo hotels which have commensurate host and guest parts. We checked the validity of our calculations by calculating the change in energy due to displacing the guest chains along the channels with respect to the host structure. Shifting the guests in our pseudo hotels is equivalent to looking at a different part of the structure. Therefore, as we have found, shifting the guests in the pseudo hotel should have no effect on the energy of the system. In order that the small pseudo hotel structure in barium appeared more stable than the hcp structure, it was necessary to include an elastic correction to account for the increased number of guests in the cell. Our calculations indicate that the correction for the large pseudo hotel structure is much smaller, and hence less significant. It would therefore be nice to do some more calculations with this larger hotel with a sufficient number of $k$-points to allow direct comparison with the hcp structure.

The electron configuration of the hotel structures has a significantly larger proportion of d electrons than the electron configurations of the structures which are stable at ambient pressure. The barium hotel typically has more than one d electron whereas the ambient pressure bcc structure has none. The difference between the electron configurations of the hotel and rhombohedral structures in bismuth is much less dramatic, but still significant. This is perhaps to be expected given the fact that the barium hotel appears at much higher pressures. Although the electron character of the barium hotel phase is significantly different to that of the ambient pressure bcc phase, it is very similar to the electron configuration of the hcp phases on either side of the hotel phase. In fact, the electron configuration is essentially the same as the calculated configuration for the hcp structure at the same volume. The energies of the hcp and hotel structures in barium are very close and the bond lengths in the two structures are also not dissimilar. It may therefore be instructive to investigate the hcp structure in bismuth and the other group-V elements.
CHAPTER 5. THE HOTEL STRUCTURE
Chapter 6

Pressure Phase Diagrams

In the previous two chapters we have studied the high pressure hotel structures of barium and of bismuth and the low pressure rhombohedral structures of bismuth and antimony. The purpose of this chapter is to study the other stable phases of these elements and to describe the transitions from one to another. In order to properly describe the experimentally stable phases it is also preferable to investigate viable alternatives. Whilst this may initially seem unnecessary it helps establish the reliability of the pseudopotential, and gives an indication on the accuracy required in the calculations.

6.1 Barium

At ambient pressure and temperature, barium has a bcc structure. As the pressure is increased to 5.5 GPa it transforms to hcp. Not unusually, the $c/a$ ratio of the hcp structure is 1.58 as opposed to the ideal value of 1.633 obtained with hard spheres. However, as barium is compressed further, this ratio reduces to just below 1.5 at 12.6 GPa where it assumes the hotel structure. On further compression it regains an hcp structure after passing through the hotel phase but with a constant $c/a$ ratio of 1.58. In this study we have been able to show that this is in fact the same hcp phase as seen at lower pressure.

For our calculations on barium we found a plane-wave cut-off energy of 350 eV was enough to converge the total energy to within 0.1 meV/atom. This error is transferable to all the Ba
structures that were investigated. Convergence tests for the k-point sampling have to be done for each structure.

### 6.1.1 bcc

Before studying in detail the experimental ground state structure, it is first necessary to determine at how many k-points we need to sample the band energies, in order to accurately represent the integral of equation 2.33. The total energy is therefore calculated using several different Monkhorst-Pack sets of k-points, and the results compared. For a primitive bcc cell of volume 63.25 Å³ the total energies calculated using irreducible k-point sets, based on meshes with 17³ cells or more, were found to agree to within 0.1 meV. As the pressure is increased so the volume of the cell decreases and the space between k-points increases. As a result more k-points should be required at higher pressure for the same degree of convergence of the total energy. Normally however, the smoothness of the band structure is assumed not to change with pressure and so the same k-point mesh is used at all pressures. Further convergence tests with a cell of volume 34.45 Å³, corresponding to a pressure of about 14 GPa, suggested that at higher pressure the convergence is not as tight as at lower pressures. However, the reduction in convergence is very small; less than 0.1 meV. For calculations done with the 17³ mesh and finer the total energy was still converged to within 0.2 meV. All further calculations of the primitive bcc cell were therefore done using a 17³ mesh which gives a total of 165 irreducible k-points.

The properties of the cell were then determined at many different pressures. To avoid the errors associated with the basis cut-off energy changing with volume, all the calculations were done at a fixed volume. A Birch-Murnaghan equation of state was then fitted to these data which gave the equilibrium volume to be 63.4±0.2 Å³. The error quoted is only that due to the fitting of the Birch-Murnaghan equation of state to the data and does not take account of other errors. This volume is only 0.15 Å³ (0.2%) greater than the experimental value of 63.25 Å³ [84]. The bulk modulus according to the fitting procedure is 8.4 GPa.

If we only fit the Birch-Murnaghan equation of state to results of simulations with pressures below about 3.5 GPa then a better fit around zero pressure is obtained. These parameters still fit the calculated values reasonably well up to around 8 GPa, after which the fit is no
longer quite so good. See figure 6.1. Since the bcc structure is the stable phase at lower pressures it is preferable that the fitted curve most accurately matches the calculations at lower pressures rather than at higher pressures where it is no longer stable. This low pressure fit gives the equilibrium volume to be $62.8 \text{ Å}^3$ and the bulk modulus to be 9.2 GPa. Whilst this volume is not as close to the experimental volume as when fitted to all the data, it is a more accurate representation of the calculations. The calculated bulk modulus is also closer to the experimental value of 9.6 GPa.

Figure 6.1: Murnaghan equations of states (lines) fitted to the calculated data for bcc barium. The dashed lines were fitted to all the available data while the solid line was only fitted to data from cells with volumes greater than about $48 \text{ Å}^3$. The right hand graph shows that the solid line is a significantly better fit than the dashed lines at low pressures (high volumes). Although the left hand graph shows that the dashed line is a better fit at high pressures, the difference is not as significant as at low pressures. Further, as the stable phase has an hcp structure at higher pressures, shown by crosses in the left hand graph, it is more important that the equation of state is better at lower pressures.

6.1.2 fcc

Experimentally barium is not known to assume an fcc structure. When investigating a system however, it is good practice to calculate the total energy of other viable structures. This helps
to verify the quality of the pseudopotential. If an unusual structure is found to be stable at a particular volume, then it is useful to be able to show that at least all the most common possible structures are less stable.

Due to the symmetry of the fcc cell, the number of \( k \)-points obtained with odd or even meshes varies considerably: a \( 16^3 \) mesh gives 409 irreducible \( k \)-points whilst a \( 17^3 \) mesh gives only 165. Since both meshes gave equally accurate results, the odd mesh was used because the number of irreducible \( k \)-points is smaller. The Birch-Murnaghan equation of state was fitted to the results of calculations with cell volumes greater than 39 Å\(^3\).

### 6.1.3 hcp

Experimentally barium is known to have two hexagonally close packed (hcp) phases labelled II and V. Whilst both have the same structure, they have different properties. Generally hcp structures are characterised by the ratio of the long side length to the short side length, denoted \( c/a \). In “ideal” hexagonally close packed structures, such as that formed by tennis balls, \( c/a \) is \( \sqrt{8/3} \approx 1.632 \). When phase II first appears at 5.5 GPa \( c/a \) is 1.58. As the pressure is increased this ratio plummets to just below 1.5 at 12 GPa after which it transforms to the hotel phase. The ratio \( c/a \) in phase V however remains constant at about 1.58 which is close but significantly less than the ideal ratio.

Our calculations of the hcp structure were done with a \( k \)-point mesh of \( 9 \times 9 \times 11 \) which is sufficiently fine so that at 51 Å\(^3\) the energy is converged to within 0.1 meV. Figure 6.2 shows the calculated variation of the \( c/a \) ratio with pressure. Initially the calculated and experimental ratios agree very well. The calculated ratio however does not decrease as fast as the experimental ratio. An advantage of these calculations is that the next 30 GPa are inaccessible experimentally. Figure 6.2 clearly shows that the hcp \( c/a \) ratio climbs gently with pressure, and is equal to the experimental value when phase V appears. The instability of the hcp structure with respect to the hotel structure is suggested by the flattening of the graph of the Fermi energy against pressure between about 12 and 45 GPa. Such a flattening could be caused by a peak in the density of states at the Fermi energy. In general, such peaks suggest that the crystal is unstable with respect to Peierls or Jahn-Teller type distortions, see section 2.13.3. The transfer
of electrons from s to d-type orbitals will leave the Fermi energy unchanged [4].

The calculated $c/a$ then seems to keep climbing towards the ideal ratio unlike the experimental result. This is probably because the pseudopotential is insufficiently accurate at these pressures. This is further suggested by the use of the new projector augmented-wave (PAW) method [48].

The PAW method is an all-electron method in that all the wave functions are correctly described everywhere. This is in contrast to the pseudopotential method which describes the valence wave functions correctly outside some radius but ignores the high frequency oscillations near the core of the atoms. In this way the PAW method resembles the linear augmented plane wave method. The PAW method however describes the wave functions as superpositions of three terms. The plane wave part correctly matches the all-electron wave function outside a certain radius, the augmentation radius. This is essentially the same as in the pseudopotential method.

As the accurate description of the wave functions near to the centre of the atoms would require a prohibitive number of plane waves, the wave functions within the augmentation radius are described using an atomic orbital basis set. The contribution to the wave functions from these atomic orbitals exactly matches the all-electron wave function within the augmentation region.
and is zero outside. The third term arises from the fact that the plane wave part also contributes to the wave function within the augmentation region. Described using atomic orbitals, the third part exactly cancels the plane wave contribution inside the augmentation region but is zero outside. This is again similar to the pseudopotential which varies slowly within the cut-off radius. In the ultra-soft pseudopotential method, the correct scattering properties of the core region are recovered by the addition of augmentation charges. In fact, the pseudopotential method can be derived from the PAW method by the adoption of a few extra approximations.

To simplify calculations, a frozen-core approximation is currently employed. The core states being imported from an isolated atom. The frozen-core approximation does however allow some mixing of states in response to the changing potential. Under the PAW method it is in principle possible to remove the frozen-core approximation and treat all the electrons self-consistently although as yet this is not done.

Although these potentials became available too late to be used very much in this thesis, it was possible to briefly study the variation of the ratio $c/a$. The results are shown in figure 6.2 and are clearly a significant improvement on the original results obtained with ultra-soft pseudopotentials. Above about 75 GPa however, the calculated ratio again diverges from that determined experimentally suggesting the limit of validity of the potentials has been reached.

The supremacy of the new PAW potentials is further illustrated by the pressure-volume relation of the hcp structure. As figure 6.3 shows, the pressure-volume relations, calculated using the PAW and ultra-soft pseudopotentials, agree with the experimental relation throughout the stability range of phase II. The relation calculated using the PAW potentials agrees significantly better with the experimental relation in phase V than the relation calculated with the ultra-soft pseudopotential.

The dramatic variation of the ratio $c/a$ can be explained in terms of electron types. As the pressure is increased there is a transfer of electrons predominately from 6s-type orbitals to 5d-type orbitals. There is also a transition of electrons from p-type to d-type orbitals. See figure 6.4. In phase V however, the 6s band is almost empty and the properties are dominated by the repulsion between the 5d electrons. Unlike the ultra-soft pseudopotential used, the Ba PAW potential treats the 5s electrons as well as the 5p and 6s electrons as valence electrons.
Figure 6.3: Variation of volume with pressure. Both sets of calculations agree well with experiment in phase II. In phase V however, the PAW results are significantly closer to the experimental values than are the ultra-soft results.

The number of s-type electrons in the PAW calculations is therefore two more than in the calculations with ultra-soft potentials. At very high pressures where all the electrons have been pushed into the core the atoms may be expected to behave like hard spheres in which case the ratio $c/a$ should be the ideal ratio of 1.632.

Zeng et al. [93] have done a detailed study using LMTO and full potential LMTO calculations, section 2.7. The results presented here generally agree with the results of their LMTO calculations. Their basis set however included f orbitals and they find a significant transfer of electrons to 5f orbitals particularly after the transition to phase V. Despite this they note that without them their results are not greatly different.

Zeng et al. have also done a more qualitative study using the simple pseudopotentials and second order perturbation theory which was first used to explain the instabilities in elements from beryllium to mercury [35]. In this model, the total energy of a system with arbitrary atomic positions $R_{ij}$ is

$$E_{\text{tot}} = f(V) + \sum_{i,j} \Phi(R_{ij}, V).$$  

6.1. BARIUM
Figure 6.4: Quantity of electrons in s, p and d orbitals as given by calculations using ultra-soft and PAW potentials. The PAW potential treats the 5s electrons as valence electrons. For a better comparison between the two sets of calculations, the dotted line is the number of s electrons in the US calculations +2. The filled shapes are the electron types in the hotel structure. The two structures have very similar proportions of the different types of electrons.

potential which has only a small dependence on the volume of the system. At short range this potential is very repulsive but describes the gentle Friedel oscillations at longer ranges. Hafner and Heine proposed a form for the pair potential which is dependent on physical properties of the system at ambient conditions. The important properties are the diameter of the repulsive core; the occurrence and position of the minimum around the nearest-neighbour distance; the amplitude and phase of the Friedel oscillations [28].

Moriarty showed [58] that, unlike calcium and strontium, barium cannot be treated as a simple metal. Ab initio calculations indicate (figure 6.4) that at a pressure of about 5 GPa, hcp barium has 1 d-type electron. It is therefore necessary to treat barium as a transition metal. Jank and Hafner created such a pseudopotential [41] as suggested by Hafner and Heine [28]. Zeng et al. found an analytic expression to nicely describe the pseudopotential of Jank and Hafner. Their expression is

$$\Phi(R) = C \cos(C_1 R) \left( \frac{R_0}{R} \right)^{12},$$

(6.2)

with the parameters $C=-35.75$ Ry, $C_1=1.15 \text{ Å}^{-1}$, $\delta=4.32$, $B=1.90$ mRy and $R_0=3.1$ Å. Using this potential we have calculated the energy of the hcp structure. Table 6.1 gives the radii of the
The energy per atom of the structure due to the pair-potential is simply

\[ e(V, \gamma) = \sum_{\text{shell}=1}^{4} n_{\text{shell}} \Phi(r_{\text{shell}}(V, \gamma)) . \]  

(6.3)

The optimum ratio \( c/a \) was found by minimising this expression with respect to \( \gamma \) using the symbolic maths package, Maple. We found that if only the first two shells of the non ideal structure were included, the optimum ratio was always equal to the ideal value of \( \sqrt{8/3} \). In order to get the correct non ideal optimum \( c/a \) ratio it was necessary to include the first four shells. For \( \gamma = \sqrt{8/3} \), the first two shells in table 6.1 are in fact one, as are the third and fourth shells. When including extra shells it is important to include a whole number of shells of the ideal structure. The resulting variation with pressure is shown in figure 6.5. Qualitatively, there is good agreement in so much as the ratio decreases and then increases again. In real barium, there is a transfer of electrons from s-type orbitals to d-type orbitals with increasing pressure. However, equation 6.2 does not take account of this. The potential was created with 1.25 s-type electrons and 0.75 d-type electrons. At very high pressure, Zeng \textit{et al.} predict ideal packing because the atoms become harder and behave like hard spheres. Figure 6.6 shows a volume-energy graph using this pair-potential. The hard sphere interactions have been modelled using

\[ \Phi(R) = \exp \left( \frac{-R}{\lambda} \right) \]  

(6.4)

with \( \lambda = 0.9 \). This was chosen so that at the volume of intersection of the hard sphere and hcp curves, the optimum ratio \( c/a \) was 1.58. This is the ratio in the real phase V. Clearly, this
only gives qualitative results. The energy of the hotel structure was calculated in a similar way to hcp except that the positions of the neighbours were taken from the results of our \textit{ab initio} calculations. The good qualitative agreement with figure 6.7 is due to the similarity in electron characteristics of the hcp and hotel structures. The bcc curve was calculated using only nearest and second nearest neighbours. Including more shells was found to produce vastly different results, probably due to the different electronic characteristics of the bcc and hcp structures.

**Figure 6.5**: Top: The analytic pair potential for barium with the positions of the shells of neighbours in the hcp structure shown by the arrows. The three horizontal lines of atoms indicate the positions at different volumes, namely 62.5 Å\(^3\) (top row) 40.0 Å\(^3\) (middle row) and 27.5 Å\(^3\) (bottom row). The long arrows are the positions of the neighbour shells in the optimum non-ideal structure whereas the short arrows indicate the corresponding positions of the shells in the ideal structure. Bottom: The optimum c/a ratio at each volume as calculated using the analytic pair potential (solid squares). For comparison, the ratios predicted by the \textit{ab initio} calculations using ultra-soft potentials (circles) and PAW potentials (squares) are also shown.

### 6.1.4 Phase transitions

Studying each phase individually is in itself interesting. However, what is often of more interest and certainly of more practical use is to study how and when these different phases appear. Plotting energy per atom against volume per atom for all the different phases indicates if and
when a particular structure should be stable and therefore experimentally visible. The structure with the lowest energy at any particular volume is the stable phase. As already discussed in section 2.14.6 the pressure at which the transition from one phase to another occurs may be determined by calculating the gradient of the line which is tangential to the energy-volume curves of both phases. The results of our calculations are shown in figure 6.7. As can be seen, the energetic differences between the various phases of barium are very small. It is therefore difficult to find the common tangents accurately. An alternative method is to study the difference in enthalpy (energy + pressure × volume) between the competing structures as a function of pressure, figure 6.7.

In our original calculations of the hotel phase, the eleven atom supercell was insufficiently close to the experimental structure to make it stable with respect to the hcp structure. The hotel supercell used contains too many guest atoms so there is an increase in energy due to forcing in these extra guests. The increase in energy due to squashing the guests into the commensurate cell may be approximated by measuring the stress $\sigma_{33}$ due to a uniaxial compression $\epsilon_{33}$. In later calculations it was possible to use a supercell containing 27 atoms with a $c_{\text{host}}/c_{\text{guest}}$ ratio of 1.4 compared to 1.39 experimentally and 1.5 in the eleven atom supercell. This improvement was sufficient to make the hotel structure stable with respect to hcp over a small range of pressures without adding an elastic correction. The elastic correction is however only 0.6 meV.
CHAPTER 6. PRESSURE PHASE DIAGRAMS

Figure 6.7: Graph of energy against volume for various phases in barium. At larger volumes bcc has the lowest energy, while hcp has lower energy at volumes smaller than 48±2 Å³. Inset shows the enthalpies of the hcp and hotel structures compared to the enthalpy of the bcc structure.

However, the k-point sampling density in the calculations of the 27 atoms cell was insufficient to accurately compare its energies with those of hcp.

Once the elastic correction has been made to the results for the 11 atom hotel our calculations predict phase transitions which are in good agreement with experiment, see table 6.2.

<table>
<thead>
<tr>
<th>transition</th>
<th>transition pressure (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>calculated</td>
</tr>
<tr>
<td>bcc → hcp</td>
<td>5</td>
</tr>
<tr>
<td>hcp → hotel</td>
<td>9.5</td>
</tr>
<tr>
<td>hotel → hcp</td>
<td>23</td>
</tr>
</tbody>
</table>

Table 6.2: Comparison between calculated and experimental transition pressures in barium
6.1. BARIUM

6.1.5 Zero-point Energies

Ab initio calculations are often described as being executed at zero pressure. Strictly speaking however, this is incorrect as the zero-point vibrational energy is neglected. This is normally accepted since they are generally small in comparison with the other sources of energy. Whilst this may be true in many cases, one of the reasons it is seldom done is the expense of the calculations required. See section 3.5. Typically large cells containing lots of atoms are required. Although in systems which are highly symmetric only one calculation may be needed to fully determine the dynamical matrix, in general for a system containing N atoms, 3N calculations are required. Once the dynamical matrix is known, the phonon density of states may be calculated and hence the zero point energy. It is also then possible to calculate other temperature dependent properties such as the Helmholtz free energy and the heat capacity of the material. If the dynamical matrix is computed at many different volumes it is then possible to calculate the Gibbs free energy. If the Gibbs energy is calculated for many different structures then it should be possible to construct a pressure-temperature phase diagram which may be compared to experiment.

With the increasing implementation of perturbation theory methods, see section 3.7, the evaluation of the zero-point energies and the pressure-temperature phase diagrams may become much more common.

The zero-point energies have been calculated for the bcc and fcc structures of barium at ambient pressure. In both cases a cubic supercell containing 9 cubic basis cells was used. The supercell for the bcc structure therefore contained a total of 54 atoms while the fcc supercell contained 108 atoms. The dynamical matrix was determined by calculating the forces due displacing the first atom by 0.005 Å which is 0.11% of the lattice parameter in the case of bcc and by 0.0033 in fcc and the forces were calculated. The force calculation was done using a $4^3$ k-point mesh as this gives the same sampling density of the Brillouin Zone in reciprocal space as the mesh used in the calculations of the primitive cell.

The dynamical matrix was then determined as described in section 3.3. In order to calculate the phonon density of states the vibrational frequencies were integrated over the whole of the Brillouin zone, see section 3.4. The sampling of the Brillouin zone was done using a $50^3$ mesh.
Monkhorst-Pack k-point mesh (section 2.13.1) giving a total of 125000 k-points. The resulting phonon density of states for the bcc and fcc structures are shown in figure 6.8. The variation of the vibrational frequencies with highly symmetric wave vectors is shown by the dispersion curves in figure 6.9. These are in excellent agreement with the experimental results presented in the theoretical study of Moriarty [58].

The zero-point energy calculated for the bcc structure is 9.6 meV whereas for the fcc structure it is 10.2 meV. As the zero-point energy for fcc is greater than that of bcc it might be expected that at some temperature there will be a bcc to fcc transition. However, the difference between the ground state energies of the two structures is about 20 meV which is much greater than the differences in the zero-point energies. At 300K the energy contributions from the phonons, including zero-point energies, has risen to 77.99 meV and 78.05 meV for the bcc and fcc structures respectively. However, the difference between the two has decreased indicating that there will not be a temperature driven transition. Ooops of course there won’t be a transition.

Another experimentally measurable quantity which can be calculated from the phonon density of states is the calculated heat capacity. At 300 K, the specific heat capacity of bcc barium is 182 Jkg$^{-1}$ K$^{-1}$ which is only 11% less than the experimental value of 204 Jkg$^{-1}$ K$^{-1}$ [89].
6.2 Group-V elements

Under ambient conditions the heaviest three group-V elements; namely antimony, arsenic and bismuth, all assume a rhombohedral structure. Bismuth transforms to a monoclinic structure at 2.55 GPa [84] and then to the hotel structure at 2.8 GPa [52] before adopting a bcc structure at 7.7 GPa [52]. Although the transition pressures and structures are well known in bismuth there is some ambiguity over the high pressure phases in antimony and arsenic. Simple-cubic phases have been observed in both elements by some experimentalists [8] but others have not been able to find them [39, 75]. In arsenic the transition has also been predicted theoretically by Mattheis et al. [50]. At 0 K our calculations prohibit a first order rhombohedral to simple-cubic transition. It is however possible for such a transition to occur at higher temperatures. See section 4.6 for further discussion on the existence of the simple cubic phases.

Our calculations on all three elements were executed with a plane-wave cut-off of 350 eV. This was found in each case to be sufficient to converge the total energy to within 0.1 meV at ambient pressure. The Brillouin zones of the rhombohedral structures were sampled using a...
Chapter 6. Pressure Phase Diagrams

A mesh of \(18^3\) giving a total of 570 irreducible \(k\)-points. This was found to be sufficient for the total energy to be converged with respect to the number of \(k\)-points to within 0.2 meV. Again, convergence tests were done separately for each element. Calculations of the simple-cubic structures in antimony and bismuth were done with \(k\)-point meshes of \(27^3\) and \(28^3\) respectively giving totals of 560 and 455 irreducible \(k\)-points. The Brillouin zone in the monoclinic phase of bismuth was sampled using a \(13^3\) mesh giving 595 irreducible \(k\)-points while that of the bcc phase was sampled using a \(23^3\) mesh giving 364 \(k\)-points. The convergence with respect to \(k\)-points of the energy in the monoclinic structure in bismuth was very slow. The energies calculated with the \(13^3\) mesh are only converged to within 2.5 meV, however it was not feasible to do calculations with a finer mesh. The bcc phase in antimony was sampled using the same mesh as in bismuth.

As usual, “production” calculations were done at constant volume under hydrostatic conditions. Both ionic and cell degrees of freedom were allowed to relax as described in section 2.14.4.

The resultant energy volume curves for antimony and bismuth are given in figures 6.10 and 6.11 respectively. It can be clearly seen in figure 6.10, that the simple cubic phase is a special case of the rhombohedral structure and therefore represents an upper bound on the energy of the rhombohedral structure. For clarity, the simple cubic phase has been omitted from figure 6.10.

![Figure 6.10](image-url)
6.3 Summary

The study of individual structures is interesting in its own right. However, the relations between the different structures and their appearance under different conditions is perhaps of more practical use. In this chapter we have studied the various phases of barium and calculated...
the pressures of the transitions between them. Our calculated pressure of the transition from
the ambient bcc phase to the first hcp phase, phase II, is in good agreement with the experiment-
tally measured value. The transitions from hcp phase II to the hotel structure and then from the
hotel to hcp phase V are in reasonable agreement with experiment but the exact values are very
dependent on the elastic correction added to the hotel structure. In this work the correction was
calculated at one pressure and used to correct the calculated energies of the the hotel structure
at all pressures. Calculations of this correction at each pressure, or better still, the use of the
bigger cell for which the correction is much smaller, should improve agreement. Performing a
more detailed study of the hcp phases also proved worthwhile. Experimentally, there are two
hcp phases, one either side of the hotel phase. Our calculations reveal that if the hotel phase
did not intervene, hcp phase II would transform continually to phase V.

The calculated transition pressures between the various phases in bismuth are between 1 GPa
and 6 GPa higher than those seen experimentally. However, they are in roughly the same
proportions. As far as predicting transition pressures using \textit{ab initio} calculations goes, our cal-
culated values are in quite good agreement with the experimental values. We have investigated
the rhombohedral phases of antimony and, elsewhere, arsenic. Our calculations of the rhombo-
hooded structure, as mentioned in chapter 4, agree well with experimental results. Further work
on the various high pressure phases would be interesting to do.
Chapter 7

Two-Band Model

In previous chapters we have seen that using ab initio calculations it is possible to accurately calculate various properties of materials. However, using these techniques, the total number of particles that it is possible to include in a calculation is very limited. For the accurate determination of the properties of metallic systems, calculations involving 50 to 100 atoms are really only feasible with super computers. Systems of this size are adequate for the calculation of phonon frequencies in systems with relatively simple crystal structures and also perhaps in systems with more complicated structures, such as the hotel phase in barium. However, in order to study the effects of lattice defects, such as dislocations and impurities, much larger systems, containing perhaps thousands of particles are required. It therefore follows that much simpler techniques are required for the study of large scale systems.

In 1984 Finnis and Sinclair [23] suggested a simple model for particle interactions in transition metals. Their model comprises an attractive part, which is a function of the positions of all the neighbouring atoms and a repulsive part, which is simply the sum of the pair-wise repulsions between atoms. Whilst the model is more complicated than a purely pair-wise potential such as that of Lennard and Jones [?], it is still relatively quick to calculate. As a result, it has been used in a wide range of applications. One of the reasons for its success is that it represents the cohesive and vacancy formation energies more accurately than the simpler pair potentials [23]. The two-band model presented here is similar to the model of Finnis and Sinclair. Both are based on Friedel’s statement that the widths of the bands are dependent on the hopping
of electrons from one atom to another. They also both use the moments theorem of Cyrot-
Lackmann [18] to calculate the widths of the bands. However, the two-band model has both
a d-band and an s-band, linked with an exchange term, whereas the Finnis-Sinclair model in-
cludes only a d-band. This should allow the study of the transition of electrons from s-type
orbits to d-type orbits as materials are squeezed. Such behaviour is seen in barium and is
also believed to be the driving force behind the large volume change during the transition be-
tween phase II and phase III in caesium. Both of these phases have long been thought to be
fcc. However, recent theoretical work by Christensen et al. [15] suggests that phase III has
been identified incorrectly. More recently McMahon et al. [?] have published results of X-ray
diffraction experiments from which they have determined that structure of phase III is a very
complicated with 80???? atoms in the unit cell!

In 1970 Hemmer and Stell [36, 81] used core softened potentials to study liquids with several
phase transitions. They also note that their potential may be used to study certain features in
real systems such as the alleged iso-structural fcc-fcc phase transitions as proposed in caesium.
The core softened potentials are often quite artificial being constructed by simply adding a
Gaussian well on to a Lennard-Jones type pair potential or even more simply, by adding a hard
core repulsion to an attractive negative tail, see figure 7.1. Hopefully, our two-band model will
provide potentials with a more physical basis and allow us to capture the behaviour of these
systems.

![Figure 7.1: The core softened potential of Stell and Hemmer [36] (left). A Lennard-Jones \( \frac{1}{r^6} - \frac{1}{r^12} \) type potential plus a Gaussian well, \( e^{-c(r-r_0)^2} \) where c is a positive constant (right).]
7.1. **COHESIVE, BAND AND BOND ENERGIES**

The equilibrium state of a system exists where the attractive forces due to the formation of bonds balance the repulsions between neighbouring atoms. The volume of the system when this balance occurs corresponds to a minimum in the cohesive energy of the system.

In solids at zero kelvin, electrons populate all the lowest available eigenstates of the system. The energy of the highest occupied state is the Fermi energy. At finite temperatures this boundary is blurred according to Fermi-Dirac statistics, see figure 7.2. To simplify matters, we will neglect the effect of finite temperature.

If the density of states is given by \( D(E) \), the energy due to the electron population is

\[
E_{\text{band}} = 2 \int_{-\infty}^{E_f} E D(E) \, dE
\]

where the factor of 2 is to account for spin degeneracy.

In isolated atoms electrons occupy discrete energy levels. In solids however, these discrete levels broaden into bands due to the hopping of electrons between neighbouring atoms. A
more interesting quantity for studying the formation of solids is therefore the bond energy, which may be written:

\[ E_{\text{bond}} = 2 \int_{-\infty}^{E_f} (E - \alpha) \, D(E) \, dE \]  

(7.2)

where \( \alpha \) is the energy of the centre of the band. In an isolated atom this is the energy of the electrons and hence \( E_{\text{bond}} \) is equal to zero. Therefore \( E_{\text{bond}} \) is solely due to the formation of bonds. It is easy to show that the bond energy is just \( E_{\text{band}} - n_e \alpha \) where \( n_e \) is the number of electrons in the band. This corresponds to a translation of the band.

The total density of states of the system may be written:

\[ D(E) = \sum_{\text{all } E_k} \delta(E - E_k) \]  

(7.3)

where \( E_k \) are the eigenstates of the system. Clearly, this gives a jagged density of states. However, in the limit of an infinite system the number of eigenstates tends to infinity while the separation becomes infinitesimally small. Hence, the density of states becomes smooth and continuous. The total density of states may be expressed as the sum of all the local densities of states on individual atoms. The local density of states is defined:

\[ d_i(E) = \sum_{\text{all } E_k} \delta(E - E_k) \langle i | \psi_k \rangle \langle \psi_k | i \rangle \]  

(7.4)

### 7.2 Moments Approximation

Many of the features of the density of states, such as its width and shape, may be predicted using the moments theorem of Cyrot-Lackmann [18]. This theorem relates these features to the arrangement of atoms in the neighbourhood of the atom under investigation. The \( p \)th moment of the local density of states is defined to be:

\[ \mu_i^{(p)} = \int_{\text{whole band}} (E - \alpha)^p \, d_i(E) \, dE \]  

(7.5)

Substituting equation 7.4 into this expression gives

\[ \mu_i^{(p)} = \int_{\text{whole band}} (E - \alpha)^p \, \sum_{\text{all } E_k} \delta(E - E_k) \, \langle i | \psi_k \rangle \langle \psi_k | i \rangle \, dE \]  

\[ = \sum_{\text{all } E_k} \int_{\text{whole band}} (E - \alpha)^p \, \delta(E - E_k) \, \langle i | \psi_k \rangle \langle \psi_k | i \rangle \, dE \]  

(7.6)
On integration, and noting that \((E - \alpha)^p\) is just a number, we obtain:

\[
\mu_i^{(p)} = \sum_{\text{all } E_k} \langle i | \psi_k \rangle (E_k - \alpha)^p \langle \psi_k | i \rangle \\
= \sum_{\text{all } E_k} \langle i | (| \psi_k \rangle E_k \langle \psi_k | - | \psi_k \rangle \alpha \langle \psi_k |)^p | i \rangle .
\]  

(7.7)

However, \(\sum_{\text{all } E_k} | \psi_k \rangle E_k \langle \psi_k |\) is just the Hamiltonian, \(H\) and \(\sum_{\text{all } E_k} | \psi_k \rangle \alpha \langle \psi_k |\) is the diagonal element \(H_{ii}\) therefore

\[
\mu_i^{(p)} = \langle i | (H - H_{ii})^p | i \rangle .
\]  

(7.8)

The zeroth moment is \(\langle i | i \rangle = 1\) due to the normalisation properties of \(\langle i | i \rangle\) and the first moment is \(\langle i | H | i \rangle - \langle i | H \alpha | i \rangle = H_{ii} - H_{ii} = 0\). The second moment can be written as \(\langle i | (H - H_{ii})(H - H_{ii}) | i \rangle\). This can be rewritten using the properties of complete basis sets as

\[
\mu_i^{(2)} = \sum_{i'} \langle i | H - H_{ii} | i' \rangle \langle i' | H - H_{ii} | i \rangle
\]  

(7.9)

where the sum \(i'\) is over all the atoms. The integrals \(\langle i | H - H_{ii} | i' \rangle\) represent the electrons hopping between atoms \(i\) and \(i'\) and these will be zero unless the atoms are close neighbours.

Also, since \(\langle i | H - H_{ii} | i \rangle = 0\) and defining \(\langle i | H - H_{ii} | i' \rangle = H_{ii'}\) for \(i \neq i'\), we can rewrite equation 7.9:

\[
\mu_i^{(2)} = \sum_{i' \neq i} H_{ii'} H_{i'i} .
\]  

(7.10)

This can be interpreted as an electron starting at atom \(i\), hopping out to atom \(i'\) and then back again giving a hop of length 2. Thus, the second moment is the sum of all the possible hops of length 2. For example, if the nearest neighbour hopping integral is \(\beta\) and atom \(i\) has \(z\) nearest neighbours then the second moment is \(z\beta^2\). This is illustrated in figure 7.3. This idea may easily be extended to higher order moments: the third moment is the sum of all the possible hops of length 3; and the \(n^{th}\) moment is the sum of all hops of length \(n\) starting and finishing at atom \(i\).

According to the moments theorem, the width of the band is proportional to \(\sqrt{\mu_i^{(2)}}\). The third moment describes how symmetrical the band is; a large negative moment suggests a long thin tail below the centre of the band with a compressed peak above. Another interesting quantity is the ratio of the fourth moment to the square of the second moment. If this quantity is greater
Figure 7.3: The moments may be expressed in terms of electrons hopping around closed paths whose length is equal to the order of the moment. Thus a) illustrates one of the six possible paths of length two giving a second moment $\mu_2 = 6\beta^2$; and b) one of the 12 routes of three hops giving a third moment of $\mu_3 = 12\beta^3$.

than two then the band has one maximum while if it is less than two then the band has two maxima.

7.3 Friedel Model

Friedel states [25] that the broadening of the d-band is due to a resonance between the atomic d-levels which allows electrons to jump from one atom to another. Thus the shape and size of the d-band depends on the values of the hopping integrals.

Consider a simple rectangular band of width W, such as the one illustrated in figure 7.4, which can contain a total of N electrons\(^1\). Following equation 7.2, the bond energy for such a band is

$$E_{bond} = \int_{\alpha-W/2}^{E_f} (E - \alpha) \frac{N}{W} dE$$

$$= \frac{N}{W} \left( \frac{1}{2} E_f^2 - \alpha E_f + \frac{1}{2} \alpha^2 - \frac{W^2}{8} \right). \quad (7.11)$$

If the band actually contains $n$ electrons then the Fermi energy is $E_f = \alpha + (\frac{n}{N} - \frac{1}{2})W$ which on substituting into equation 7.11 gives

$$E_{bond} = \frac{W}{2N} n(n - N) \quad (7.12)$$

which is independent of $\alpha$.

To make use of this bond energy we need to build a simple model of cohesion. We can do this\(^1\) including the factor of 2 to account for spin degeneracy.
7.4. THE TWO-BAND MODEL

by simply adding a term which describes the repulsion between the atoms:

\[ E_{coh} = E_{bond} + E_{rep} . \] (7.13)

Given an appropriate parametrisation of the band width and the repulsive component, this is essentially the Finnis-Sinclair model.

7.4 The Two-Band Model

The above model has been successfully used to study a large variety of systems. However, we are interested in systems in which electrons change from one type of orbit to another and in particular, from an s-type orbital to a d-type orbital as the sample is pressurised.

Consider therefore two rectangular bands of widths \( W_1 \) and \( W_2 \) as shown in figure 7.4. The bond energy of an atom may be written as the sum of the bond energies of the two bands on that atom as in equation 7.12, and a third term giving the energy of promotion from band 1 to band 2:

\[ E_{bond} = \frac{W_1}{2N_1} n_1(n_1 - N_1) + \frac{W_2}{2N_2} n_2(n_2 - N_2) + E_{promotion} , \] (7.14)

where \( N_1 \) and \( N_2 \) are the capacities of the bands and \( n_1 \) and \( n_2 \) are the numbers of electrons actually in each band. The sum of the numbers of electrons in each band is necessarily constrained to be equal to the total number of electrons on an atom, \( T \). The difference between the
CHAPTER 7. TWO-BAND MODEL

energies of the band centres $\alpha_1$ and $\alpha_2$ is assumed to be fixed. The values of $\alpha$ correspond to the appropriate energy levels in the isolated atom. Thus, $\alpha_2 - \alpha_1$ is the excitation energy from one level to another. The promotion energy term is therefore simply

$$E_{promotion} = n_2(\alpha_2 - \alpha_1) = n_2E_0,$$  \hspace{1cm} (7.15)
on defining $E_0 = \alpha_2 - \alpha_1$.

Equation 7.14 contains two coupled unknown variables which is not very convenient. Since the total number of electrons on an atom, $T = n_1 + n_2$ is fixed, we can define a new single independent variable $\eta = n_1 - n_2$ which is the difference in the occupation of the two bands. This new variable specifies the distribution of electrons between the two bands. Rewriting equation 7.14 in terms of the electron distribution, $\eta$:

$$E_{bond} = -\frac{\eta}{4}(W_1 - W_2) - \frac{T}{4}(W_1 + W_2) + \frac{\eta^2 + T^2}{8} \left( \frac{W_1}{N_1} + \frac{W_2}{N_2} \right) + \frac{\eta T}{4} \left( \frac{W_1}{N_1} - \frac{W_2}{N_2} \right) + \frac{T - \eta}{2}E_0.$$  \hspace{1cm} (7.16)

Having obtained an expression for the bond energy, it is now necessary to develop an expression for the cohesive energy. As before (see equation 7.13) the cohesive energy is the bond energy plus a repulsive term. Since there are two different types of bands, it is necessary to have two different repulsive terms. The amount of each repulsion is dependent on the occupations of the two bands. The number of electrons in band 1 is, in terms of the electron distribution, $\frac{1}{2}(T + \eta)$. Similarly, the number of electrons in band 2 is $\frac{1}{2}(T - \eta)$. The cohesive energy of an atom is therefore

$$E_{coh} = E_{bond} + \frac{1}{2}(T + \eta)E_{rep}^A + \frac{1}{2}(T - \eta)E_{rep}^B.$$  \hspace{1cm} (7.17)

The electron distribution $\eta$, on an atom is that which minimises the cohesive energy of that atom, equation 7.17. The optimum electron distribution may therefore be obtained by solving

$$\frac{dE_{coh}}{d\eta} = 0$$  \hspace{1cm} (7.18)

for $\eta$. On doing so we get the optimum electron distribution to be:

$$\eta_0 = \frac{N_1N_2}{W_1N_2 + W_2N_1} \left[ W_1 - W_2 - T \left( \frac{W_1}{N_1} - \frac{W_2}{N_2} \right) + 2E_0 - 2E_{rep}^A + 2E_{rep}^B \right].$$  \hspace{1cm} (7.19)
However, depending on the number of electrons in the system it may not be possible to realise this state. It is therefore necessary to limit the values that $\eta$ may have:

$$\eta = \begin{cases} 
\min(T, 2N_1 - T), & \text{if } \eta_0 > \min(T, 2N_1 - T) \\
\max(-T, T - 2N_2), & \text{if } \eta_0 < \max(-T, T - 2N_2) \\
\eta_0, & \text{otherwise}
\end{cases}$$  \hspace{1cm} (7.20)

where $\eta_0$ is given by equation 7.19.

## 7.5 Implementation

For the two-band model to be of any practical use, it needs to be parametrised for use in real systems with atoms in arbitrary positions. In general, each atom has a different arrangement of neighbours. As a result, the widths of the bands and hence the distribution of electrons between the bands will vary from atom to atom. The local electronic distribution $\eta_i$, is that which minimises the cohesive energy of the individual atom according to equations 7.18 and 7.20. The local depends only on the position, or rather more the proximity of the neighbouring atoms. The local density of states of one atom is independent on the local densities of its neighbours. Similarly, the cohesive energy of an atom depends only on the proximity of the neighbouring atoms and not on any of their other properties. The cohesive energy of the system $E_{coh}$, may therefore be written as the sum of the cohesive energies of the individual atoms:

$$E_{coh} = \sum_i E_{coh_i}(\eta_i),$$  \hspace{1cm} (7.21)

where the sum is over all the atoms in the system and the cohesive energy of atom $i$ $E_{coh_i}$, is given by equation 7.17.

Having split the cohesive energy of the system into the sum of the cohesive energies of the individual atoms, it is necessary to parametrise the band widths and also the interatomic repulsions. According to the moments theorem, the width of a band is given by the square root of the nearest neighbour hopping integrals. These hopping integrals can be parametrised by a pair potential. We have adopted a cubic form for the square of the nearest neighbour hopping
The hopping integral for the b-band on atom $i$, $\phi_{ib}$ is:

$$\phi_{ib}(r_{ij}) = \begin{cases} 
C_b(d_b - r_{ij})^3, & \text{if } r_{ij} \leq d_b \\
0, & \text{if } r_{ij} > d_b 
\end{cases} \quad (7.22)$$

where $r_{ij}$ is the distance from the $i$th to the $j$th neighbour, $|r_j - r_i|$. The subscript $b$ is to distinguish between the functions and parameters of the different bands. The range, $d_b$, is an extra parameter which we take to be between the second and third nearest neighbours for the first band and between the first and second neighbours for the second band. The parameters $C_b$ are free for fitting to the experimental data. Both the $C_b$’s and the ranges are constants and are the same for all atoms. The advantage of choosing this form for $\phi$ is that the function and its first and second derivatives are continuous and smooth. The cubic form is also simpler and quicker to evaluate than exponential forms. The width of a band is then given by

$$W_{ib} = \sqrt{\sum_j \phi_{ib}(r_{ij})}. \quad (7.23)$$

The repulsive pair potentials were parametrised with a Van der Walls type $r^{-12}$ function. These were found to be much easier to fit to the experimental data than exponential terms. The repulsive terms were simply:

$$E_{rep_i}^b = A_b \sum_j \frac{1}{r_{ij}^{12}} \quad (7.24)$$

where the parameters $A_b$ are free for fitting to experimental data. Once the band widths and the repulsive terms of atom $i$ are known, the distribution of the electrons $\eta$ may be found by substituting $W_{i1}, W_{i2}, E_{rep_i}^A$ and $E_{rep_i}^B$ into equations 7.19 and 7.20.

Finally, the cohesive energy of atom $i$ is given by

$$E_{coh_i} = -\frac{\eta_i}{4} (W_{i1} - W_{i2}) - \frac{T}{4} (W_{i1} + W_{i2})$$
$$+ \frac{\eta_i^2 + T^2}{8} \left( \frac{W_{i1}}{N_1} + \frac{W_{i2}}{N_2} \right) + \eta_i T \left( \frac{W_{i1}}{N_1} - \frac{W_{i2}}{N_2} \right) + \frac{T - \eta_i}{2} E_0$$
$$+ \frac{1}{2} (T + \eta_i) E_{rep_i}^A + \frac{1}{2} (T - \eta_i) E_{rep_i}^B \quad (7.25)$$

and the cohesive energy of the system is

$$E_{coh} = \sum_i E_{coh_i}. \quad (7.26)$$
In practice, the procedure for calculating the cohesive energy of the system may be broken down into stages. Given a set of atomic positions \( \{ r_j \} \), the cohesive energy of atom \( i \) may be found as follows:

1. Evaluate the band widths \( W_{i1} \) and \( W_{i2} \) which depend on \( \{ r_j \} \)
2. Evaluate the repulsive terms \( E_{rep_i}^A \) and \( E_{rep_i}^B \) which also depend on \( \{ r_j \} \)
3. Evaluate \( \eta_0 \) according to equation 7.20
4. Determine the actual distribution \( \eta \) from equation 7.20
5. Calculate the cohesive energy of atom \( i \) using equation 7.25

The cohesive energy of the system is then simply the sum of the cohesive energies of each atom.

For Monte Carlo simulations, it is sufficient to know the cohesive energy as a function of the atomic positions. However, in order to do molecular dynamics simulations, expressions are required for the forces on the atoms. The forces are the derivatives of the energy with respect to particle position. The force on the \( i^{th} \) atom at position \( r_i \) is

\[
\mathbf{f}_i = -\frac{\partial E_{coh_i}}{\partial r_i}.
\] (7.27)

The cohesive energy is however a function not only of position but also of the electron distributions \( \{ \eta_j \} \). Displacing atoms will cause a change in the local environment of the atoms and therefore the electron distributions will change. The cohesive energy of the system is the sum of the cohesive energies of each of the atoms. The force on atom \( i \) therefore becomes

\[
\mathbf{f}_i = -\sum_j \frac{\partial E_{coh_j}}{\partial r_i} = -\sum_j \left( \frac{\partial E_{coh_j}}{\partial r_i} + \frac{\partial E_{coh_j}}{\partial \eta_j} \frac{\partial \eta_j}{\partial r_i} \right).
\] (7.28)

The electron distribution on each atom is chosen so as to minimise the cohesive energy of that atom. The derivative of the cohesive energy with respect to the electron distribution \( \frac{\partial E_{coh_i}}{\partial \eta_i} \), is therefore zero. This is analogous to the Hellmann-Feynman theorem for the \textit{ab initio} calculations which says that the derivative of the energy with respect to the wave functions is zero, see section 2.14.1. The force on atom \( i \) is therefore simply

\[
\mathbf{f}_i = -\sum_j \frac{\partial E_{coh_j}}{\partial r_i} = -\frac{\partial E_{coh_i}}{\partial r_i}.
\] (7.29)
CHAPTER 7. TWO-BAND MODEL

The independence of the forces from the electron distribution is one of the key requirements for the two-band model to produce a usable potential. Two other important factors are the ability to decompose the cohesive energy of the system into the sum of the cohesive energies of each atom and also to express the electron distribution of one atom independently of the electron distributions of its neighbours. If however, the electron density of one atom was dependent on another, then fully self-consistent calculations would be required as in the full \textit{ab initio} methods. Also, if the Hellmann-Feynman type argument did not hold then the derivative of $\eta_0$ with respect to the atomic positions would have to be calculated which would be very nasty although not impossible.

Since the forces are independent of the electron distribution $\eta$, they can be evaluated by summing pair-wise potentials as in the calculation of the energy. The force on atom $i$ is given in terms of the numbers of electrons in each band by

$$f_i = -\sum_{j \neq i} \left[ (\Omega_{i1} + \Omega_{j1}) \phi'_1(r_{ij}) + (\Omega_{i2} + \Omega_{j2}) \phi'_2(r_{ij}) 
+ (n_{i1} + n_{j1}) V'_1(r_{ji}) + (n_{i2} + n_{j2}) V'_2(r_{ji}) \right] \hat{r}_{ij}$$

with

$$\Omega_{ib} = \frac{n_{ib}(n_{ib} - N_b)}{2N_b W_{ib}}.$$  \hfill (7.31)

\(\hat{r}_{ij}\) is a unit vector from atom $i$ to atom $j$ and the primes denote the derivatives with respect to $r$. A derivation of this equation may be found in appendix B.

7.6 Fitting to caesium

In order to make the potential usable, the model was fitted to experimental data for caesium. Although a program was written to fit the parameters to the experimental data using both conjugate gradients and least squares algorithms [71, 61], they were ineffectual. As the program was unable to produce sensible results, Maple was used to fit each band separately. The resulting values for the parameters were then manipulated by hand so that the iso-structural transition pressure was correct (4.22 GPa [49]) and the global minimum was at the minimum volume for the fcc structure as predicted by VASP. This volume is within 2 Å$^3$ of the equilibrium volume.
7.6. FITTING TO CAESIUM

<table>
<thead>
<tr>
<th></th>
<th>band 1</th>
<th>band 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_s$</td>
<td>0.05617 eVÅ⁻³</td>
<td>0.1681 eVÅ⁻³</td>
</tr>
<tr>
<td>$d_s$</td>
<td>9.5097 Å</td>
<td>6.9189 Å</td>
</tr>
<tr>
<td>$A_s$</td>
<td>$2.4017 \times 10^7$ eVÅ¹²</td>
<td>$3.7668 \times 10^6$ eVÅ¹²</td>
</tr>
<tr>
<td>$E_0$</td>
<td>1.19 eV</td>
<td></td>
</tr>
</tbody>
</table>

Table 7.1: Parameters for the two-band model, obtained by fitting to phases I, II and III of caesium.

for the bcc phase (116 Å³ [49]) which is the experimental ground state structure. In the ab initio calculations the fcc and bcc phases were in fact essentially indistinguishable. The final set of parameters is that which satisfies these two criteria and whose volume collapse through the fcc-fcc transition is as close as possible to that seen experimentally. The final set of parameters was ultimately chosen since its cohesive energy was the closest to the experimental value of -0.704 eV/atom. This value was obtained by adding the heats of fusion and vaporisation from reference [49]. The bulk modulus is about 50% larger than that viewed experimentally (2.2 GPa []), however this is due to the early onset of the volume contraction and is actually in reasonable agreement.

The promotion energy $E_0$ was chosen to be equal to the energy of promotion of an electron from the 6s energy level to the 5d level [49, 7]. The values of the ranges $d_b$ in the hopping integrals were chosen to be between the second and third nearest neighbours for the s-band and between the first and second nearest neighbours for the d-band. The actual values used were chosen so that the transition pressure was as close as possible to the experimentally observed pressure.

The final parameters are given in table 7.1, and figure 7.5 shows the energy-volume curves for the fcc and bcc structures calculated using the model. Experimentally however, caesium phase I has a bcc structure with an equilibrium volume of 116 Å³. It is perhaps unfortunate that this potential does not have a low pressure bcc phase, but it is not surprising since no information about caesium phase I was provided and since ab initio simulations are also unable to correctly resolve the difference. The predicted equilibrium volume is in good agreement with the equilibrium volume for the fcc structure calculated with VASP and is also very close
to the experimental equilibrium volume of the bcc phase. The volume collapse starts at 77.6 Å\(^3\) which is similar to the experimental volume of phase II (71.6 Å\(^3\)). The magnitude of the volume collapse is essentially equal to the difference in volume between the experimental phases II and III. The transition pressure is the same as that seen experimentally.

![Energy-volume curve for the two-band potential](image)

Figure 7.5: An energy-volume curve for the two-band potential. The gradient of the straight line is the experimental transition pressure. The top graph shows the variation of the electron distribution and illustrates the transfer of electrons from the s band to the d band with increasing pressure (from right to left).

7.7 Elastic stabilities

The mechanical stability of structures may be investigated by studying the elastic constants. A significant amount of time has been spent on such investigations over the years. The onset of structural instabilities and phase transitions are often heralded by the violation of certain stability criteria which were first introduced by Born [9]. The elastic constants also determine the acoustic velocities. However, the original theory was developed explicitly for crystals under ambient pressure. The elastic constants calculated under such conditions are, despite differing notations, generally unambiguous. However, there is much confusion over the generalisation of the theory to non-ambient conditions and over the notations. The generalisation to arbitrary
stress has been treated by various authors [86, 44, 87] but they are unclear about the exact nature of the calculations required. What follows therefore is an attempt to elucidate the subject. The ultimate aim however, is to provide a useful set of criteria with which to study the two-band model.

### 7.7.1 Definitions of the elastic constants

The elastic constants, $C_{ijkl}$, are usually defined in terms of the second derivative of the Helmholtz free energy, $F$, with respect to the infinitesimal Eulerian strain, $\varepsilon_{ij}$

$$C_{ijkl} = \frac{1}{V_0} \frac{\partial^2 F}{\partial \varepsilon_{ij} \partial \varepsilon_{kl}}. \quad (7.32)$$

where $V_0$ is the volume of the unstrained system.

In systems under an applied hydrostatic pressure however, the important energetic quantity is the Gibbs free energy and not the Helmholtz free energy. At ambient pressure, the two quantities are of course identical. The Gibbs free energy is

$$G = U - TS + PV = F + PV. \quad (7.33)$$

The elastic constants may be written in terms of the Gibbs free energy as follows:

$$C_{ijkl} = \frac{1}{V_0} \frac{\partial^2 F}{\partial \varepsilon_{ij} \partial \varepsilon_{kl}} = \frac{1}{V_0} \frac{\partial^2 G}{\partial \varepsilon_{ij} \partial \varepsilon_{kl}} - \frac{1}{V_0} \left[ P \frac{\partial^2 V}{\partial \varepsilon_{ij} \partial \varepsilon_{kl}} + 2 \frac{\partial P}{\partial \varepsilon_{ij}} \frac{\partial U}{\partial \varepsilon_{kl}} + v \frac{\partial^2 P}{\partial \varepsilon_{ij} \partial \varepsilon_{kl}} \right]. \quad (7.34)$$

If the hydrostatic pressure is applied by an external mechanism, it will be independent of the strained state of the crystal. The last two terms will therefore be zero. Consequently,

$$C_{ijkl} = \frac{1}{V_0} \frac{\partial^2 G}{\partial \varepsilon_{ij} \partial \varepsilon_{kl}} - \frac{P}{V_0} \frac{\partial^2 V}{\partial \varepsilon_{ij} \partial \varepsilon_{kl}}. \quad (7.35)$$

If the basis vectors of the strained system are given in the matrix $\tilde{b}_0$, then the matrix of the basis vectors of the strained system is

$$\tilde{b} = \left( \tilde{I} + \tilde{\varepsilon} \right) \tilde{b}_0. \quad (7.36)$$
In terms of the volume of the unstrained system, $V_0$, the volume of the strained system is

$$V = V_0 \left( 1 + \varepsilon_{11} + \varepsilon_{22} + \varepsilon_{33} + \varepsilon_{11} \varepsilon_{22} + \varepsilon_{11} \varepsilon_{33} + \varepsilon_{22} \varepsilon_{33} - \varepsilon_{12} \varepsilon_{21} - \varepsilon_{13} \varepsilon_{31} - \varepsilon_{23} \varepsilon_{32} \right) + \mathcal{O}(\varepsilon^3)$$

$$= V_0 \left( 1 + \sum_{i=1}^{3} \varepsilon_{ii} + \frac{1}{3} \sum_{i=1}^{3} \sum_{j=1}^{3} \sum_{k=1}^{3} \sum_{l=1}^{3} (2\delta_{ij}\delta_{kl} - \delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk}) \varepsilon_{ij} \varepsilon_{kl} \right) + \mathcal{O}(\varepsilon^3) .$$

(7.37)

Putting this into equation 7.35 gives

$$\frac{1}{V_0} \frac{\partial^2 F}{\partial \varepsilon_{ij} \partial \varepsilon_{kl}} = \frac{1}{V_0} \frac{\partial^2 G}{\partial \varepsilon_{ij} \partial \varepsilon_{kl}} - \frac{P}{2} \left( 2\delta_{ij}\delta_{kl} - \delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk} \right) .$$

(7.38)

The middle term is known as the elastic stiffness tensor. In references [86] and [44] this is denoted by $B_{ijkl}$ and $c_{ijkl}$. However, to avoid confusion with other quantities we will use $\kappa_{ijkl}$.

$$\kappa_{ijkl} = \frac{1}{V_0} \frac{\partial^2 G}{\partial \varepsilon_{ij} \partial \varepsilon_{kl}} = \frac{1}{V_0} \frac{\partial^2 f}{\partial \varepsilon_{ij} \partial \varepsilon_{kl}} + \frac{P}{2} \left( 2\delta_{ij}\delta_{kl} - \delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk} \right) .$$

(7.39)

Thus, the elastic stiffness coefficients are related to the elastic constants by

$$\kappa_{ijkl} = C_{ijkl} + \frac{P}{2} \left( 2\delta_{ij}\delta_{kl} - \delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk} \right) .$$

(7.40)

The elastic stiffness tensor, $\kappa_{ijkl}$, is highly symmetric, displaying the complete Voigt symmetry since it originates from the second derivative of the Gibbs free energy. Thus $\kappa_{ijkl}$ is symmetric under the exchange of $(i,j)$, $(k,l)$ and $(ij,kl)$. That is,

$$\kappa_{ijkl} = \kappa_{jikl} = \kappa_{ijlk} = \kappa_{klij} .$$

(7.41)

This symmetry allows the elastic constant tensor to be written with only two indices. Pairs of cartesian indices are replaced as follows

$$ij = 11 22 33 32 or 23 31 or 13 21 or 12$$

$$\alpha = 1 2 3 4 5 6$$

In Voigt notation, the elastic constants take the completely symmetric form

$$\kappa_{\alpha \beta} = \kappa_{\beta \alpha} \quad \text{with} \quad (\alpha, \beta = 1, 2, ..., 6)$$

(7.42)

In general, the elastic constants $C_{ijkl}$ do not show the proper Voigt symmetry unless the crystal is under ambient pressure and at zero temperature, in which case they are identical to the generalised elastic constants $\kappa_{ijkl}$.
The Voigt notation may also be used to describe the strain applied to the crystal. Using Voigt notation, the matrix representation of the strain tensor is written as

\[ \varepsilon = \begin{pmatrix} e_1 & e_6/2 & e_5/2 \\ e_6/2 & e_2 & e_4/2 \\ e_5/2 & e_4/2 & e_3 \end{pmatrix} . \]  

(7.43)

### 7.7.2 Born stability criteria

The Born elastic stability criteria restrict what values various moduli may have if the crystal is to be stable. They are obtained by expanding the internal free energy as a function of the strain and specifying the convexity of the energy surface [9]. Due to the Voigt symmetry, the elastic constant tensor has in general only 21 independent components. In cubic crystals however this number is further reduced by symmetry to 3, namely \( \kappa_{11}, \kappa_{12} \) and \( \kappa_{44} \). Consequently, there are three common stability criteria which impose lower bounds on the bulk, shear and tetragonal shear moduli of cubic crystals. These may be written in Voigt notation:

\[ \frac{1}{3}(\kappa_{11} + 2\kappa_{12}) > 0, \quad \kappa_{44} > 0 \quad \text{ and } \quad \frac{1}{2}(\kappa_{11} - \kappa_{12}) > 0 . \]  

(7.44)

It has been suggested that these criteria are only valid for the stability analysis of the unstressed lattice. However, if the proper generalised elastic constants, \( \kappa_{ijkl} \) as described above are used, then these criteria are valid for systems under arbitrary stress [44, 86]. For a system under hydrostatic pressure \( P \), the stability criteria may be written in terms of the second derivatives of the energy and the corrections given in equation 7.40 as follows

\[ \frac{1}{3}(C_{11} + 2C_{12} + 2P) > 0, \quad C_{44} - \frac{P}{2} > 0 \quad \text{ and } \quad \frac{1}{2}(C_{11} - C_{12} - P) > 0 , \]  

(7.45)

where

\[ \kappa_{11} = C_{11} , \quad \kappa_{12} = C_{12} + P \quad \text{ and } \quad \kappa_{44} = C_{44} - \frac{P}{2} . \]  

(7.46)

### 7.7.3 Ab initio calculation of elastic stiffness coefficients

The definition of the elastic coefficients involves the infinitesimal Eulerian strain applied to the system. When doing \textit{ab initio} calculations, however, it is usual and in fact necessary to
make finite Lagrangian strains. In this section we derive relationships between the change in
the Helmholtz free energy of the system due to Lagrangian strains and the elastic stiffness
coefficients. At 0K, the temperature of \textit{ab initio} calculations, the Helmholtz free energy is the
same as the internal energy. It is this internal energy that is calculated in \textit{ab initio} calculations.

The change in Helmholtz free energy due to applying a finite strain, $\Delta F$ can be expressed in
terms of the partial derivatives with respect to strain:

$$\Delta F = F - F_0 = \sum_{i=1}^{3} \sum_{j=1}^{3} \varepsilon_{ij} \frac{\partial F}{\partial \varepsilon_{ij}} + \frac{1}{2} \sum_{i=1}^{3} \sum_{j=1}^{3} \sum_{k=1}^{3} \sum_{l=1}^{3} \varepsilon_{ij} \varepsilon_{kl} \frac{\partial^2 F}{\partial \varepsilon_{ij} \partial \varepsilon_{kl}}, \quad (7.47)$$

where

$$\frac{\partial^2 F}{\partial \varepsilon_{ij} \partial \varepsilon_{kl}} = V_0 \ C_{ijkl}. \quad (7.48)$$

Expressions for the elastic constants may then be obtained by rearranging this equation. In
practice however, this is of little use since it involves an unknown linear term in the strain.
Even if $\partial F / \partial \varepsilon_{ij}$ were known explicitly, expressions derived from this formula would still be
useless since they diverge as $\varepsilon_{ij} \to 0$. This problem is easily solved by calculating the changes
in energy due to applying a pair of strains of equal magnitude but opposite signs. The basis
sets for the strained crystals are

$$\tilde{b}_+ = \left( \mathbf{I} + \tilde{\varepsilon} \right) \tilde{b}_0 \quad \text{and} \quad \tilde{b}_- = \left( \mathbf{I} - \tilde{\varepsilon} \right) \tilde{b}_0. \quad (7.49)$$

If the change in energy due to the positive strain is $\Delta F_+$ and that due to the negative strain is
$\Delta F_-$, then expressions for the elastic constants may be found by rearranging

$$\Delta F_+ + \Delta F_- = \sum_{i=1}^{3} \sum_{j=1}^{3} \sum_{k=1}^{3} \sum_{l=1}^{3} \varepsilon_{ij} \varepsilon_{kl} V_0 \ C_{ijkl}. \quad (7.50)$$

The same problem and solution arises when trying to calculate the elastic stiffness coefficients,
$\kappa$. However, once the elastic constants have been found, the elastic stiffness coefficients may
be calculated easily using equation 7.40.

If the crystal being investigated has internal degrees of freedom which are not fixed by the
symmetry of the cell, these should be re-optimised for the deformed cell before calculating the
change in energy.
7.7. Elastic Stabilities

7.7.4 Application of the two-band model

We have calculated the bulk, shear and tetragonal shear moduli in order to try to get some more information about the stability of the two phases and the transition from one to the other. The three moduli were determined by applying pairs of small strains to the crystal. The change in energy was then used to determine the elastic constants $C_{ijkl}$ which were then corrected to account for the applied pressure to give the elastic stiffness coefficients $\kappa_{ijkl}$.

The non zero elements of the strain in Voigt notation (see equation 7.43) required to calculate the shear modulus, $\kappa_{44}$, are $e_6 = e$ and $e_3 = e^2/(4 - e^2)$. Substitution into equation 7.50 gives

$$\kappa_{44} = C_{44} - \frac{P}{2} = \lim_{e \to 0} \frac{4(\Delta F_+ - \Delta F_-)}{Ve^2} - \frac{P}{2},$$

ignoring terms of third order and higher. The limit arises since the definition of the elastic constant involves Eulerian (infinitesimal) strains whereas in practice it is necessary to make Lagrangian (finite) strains. Normally these limits are found by making several strains of decreasing size and extrapolating back to zero. However, due to the large number of extrapolations that would be required, the following calculations were done with a value of $e$ chosen so that there was no apparent change in the moduli if $e$ was decreased further.

Similarly, the non zero elements of the strain required to calculate the tetragonal shear modulus, $1/2 (\kappa_{11} - \kappa_{12})$, are $e_1 = -e_2 = e$ and $e_3 = e^2/(1 - e^2)$ [53]. The tetragonal shear modulus is then

$$\frac{1}{2} (\kappa_{11} - \kappa_{12}) = \frac{1}{2} (C_{11} - C_{12} - P) = \lim_{e \to 0} \frac{\Delta F_+ + \Delta F_-}{4Ve^2} - \frac{P}{2}. \tag{7.52}$$

Finally, the strain required to calculate the bulk modulus, $B$, simply has $e_1 = e_2 = e_3 = e$ with the other components being zero. Equation 7.50 leads to the following expression for the bulk modulus

$$B = \frac{1}{3} (\kappa_{11} + 2\kappa_{12}) = \frac{1}{3} (C_{11} + 2C_{12} + 2p) = \lim_{e \to 0} \left( \frac{\Delta F_+ + \Delta F_-}{6Ve^2} \right) + \frac{2P}{3}. \tag{7.53}$$

In the fcc crystal of the two-band model, the three quantities are positive at the equilibrium volume of 115 Å³ indicating that the fcc structure is mechanically stable. The bulk modulus is
5.4 GPa, the tetragonal shear is 1.6 GPa and the shear constant is 20.0 GPa. As the pressure is increased, all three grow in magnitude until the volume has shrunk to about 80 Å³ at which point the bulk modulus starts to soften slightly. As the softening of the bulk modulus increases, the iso-structural transformation occurs. The shear and tetragonal shear moduli also soften but only once the transition is under way. Neither become negative. All three quantities are larger after the transition than before.

Figure 7.6: The variation of the elastic constants with pressure. The total energy per atom is also shown (dotted line, right hand axes) for comparison as is the common tangent (dash dotted line) which shows the coexistence volumes of the two phases. \( V_0 \) is the equilibrium volume of 115 Å³.

7.8 Applications

The two-band potential was incorporated into a computer program for doing lattice-switch Monte-Carlo in the NPT (constant number, isothermal and isobaric) ensemble [11] by James Magee. This program is normally used to determine the coexistence between crystalline phases and has successfully been applied to both hard sphere and Lennard-Jones potentials [40].

As time evolves the Monte Carlo algorithm proposes displacements of particles. If the displacement causes a decrease in the total energy of the system, the displacement is accepted. If however the total energy is increased, the displacement may still be accepted but with a probability which decreases as the change in energy increases. The probability of acceptance of
7.8. APPLICATIONS

An unfavourable move is larger at higher temperatures. The probability of acceptance is proportional to $e^{-\Delta E/k_BT}$. If the move is rejected, the particle is returned to its previous location before the next move is chosen. Alternative moves involving all the particles, such as changing the volume of the system, are also possible. The lattice-switch mechanism also allows the simultaneous comparison of the stabilities of various different structures. Transformations are defined which allow one structure to change into another. These moves may not always be possible and so, as with the other moves, they may be accepted or rejected.

The calculations of Magee showed that the two-band system has two stable fcc structures with significantly different equilibrium volumes. Although these phases exist at different pressures, there was insufficient time to accurately determine the pressure at which the transition from one to the other occurs.

7.8.1 Defects

One of the major features of many-body and embedded atom type potentials is their ability to describe defects such as surfaces, vacancies and interstitials without the constraints of pair potentials, for which the undercoordination defect energy is simply the sum of broken bond energies, less a small amount from relaxation of atomic positions. Thus the vacancy formation energy is typically the same as the cohesive energy, whereas in real materials it is typically less than half. The present potential is not fitted to any defect configuration, so it is of interest to see what it predicts - moreover the variety of environments associated with defects provides a good check against pathologies.

The relaxed surface energies for four low-energy surfaces are given in table 7.2. As is usual with many-body potentials the energy is much lower than would be expected from simple bond counting. For the (111) surface the energy for each atom in the plane is increased by about $1/9E_{coh}$, while each atom has 1/4 of its bonds broken.

Likewise the vacancy formation energy is 0.44eV and the vacancy formation volume $0.846V_0$, again rather typical of many-body potential results.

The interstitial formation energy is especially low, around 1.37eV depending on the orientation and the amount of relaxation allowed locally, meaning that thermal interstitial formation is
possible. This low value is due to the transfer of electrons from s- to d-band on the interstitial atom or dumbbell, similar to the high pressure behaviour.

For a detailed study of point defects in Caesium, it would be appropriate to reparameterized the potential with point defects included in the fitting, but the good results obtained here without such fitting suggest that the present model contains the right physics.

### 7.9 Extension to Iron

Iron is another interesting application of the two-band model. Since iron is magnetic, ordinary pair potentials and many-body potentials cannot predict the correct ground state structure. *Ab initio* calculations show that if the ground state structure is to be correctly predicted, the spin interactions need to be correctly accounted for. If the spin interactions are not included, the ground state is predicted to have an fcc structure instead of a bcc structure. This inability to accurately describe iron poses serious problems for the study of large systems involving iron, such as the earth’s interior. The following gives the basic formulation for a relatively simple many-body potential which should correctly describe the magnetic character of iron.

To be applicable to iron, the model developed hitherto requires some modifications. The differences arise due to the inherent symmetry of the spin-up and spin-down bands in the system. This model will not however, be able to differentiate between ferromagnetic and antiferromagnetic states.

The two bands in our magnetic model are therefore equivalent, differing only by the type of electrons occupying them. Since the bands have the same widths and capacities we can drop

<table>
<thead>
<tr>
<th>surface</th>
<th>energy meV/Å²</th>
<th>relaxation 1Å</th>
<th>relaxation 2Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>111</td>
<td>6.621</td>
<td>-0.042</td>
<td>0.000</td>
</tr>
<tr>
<td>001</td>
<td>7.599</td>
<td>-0.046</td>
<td>-0.007</td>
</tr>
<tr>
<td>011</td>
<td>8.313</td>
<td>-0.084</td>
<td>-0.006</td>
</tr>
<tr>
<td>211</td>
<td>7.908</td>
<td>-0.122</td>
<td>-0.045</td>
</tr>
</tbody>
</table>

Table 7.2: Surface energies, and atomic relaxations of the top two layers in angstroms
some of the indices used previously. Thus the bond energy in equation 7.16 of the $i^{th}$ atom becomes simply

$$E_{\text{bond}_i} = -\frac{T}{2} W_i + \frac{\mu_i^2}{4} W_i + E_{\text{promotion}_i}$$  \hfill (7.54)

where the electron distribution $\eta$ is now the magnetisation of the atom and is therefore labelled $\mu_i$. The promotion energy is again the energy gained due to transferring an electron from one band to another, however, it is different from that suggested in the previous model. Pauli’s exclusion principle forces electrons of the same spin to keep apart and this lowers the Coulomb energy. However, in order for them to stay apart the electrons must occupy higher energy states thus increasing their kinetic energy. The optimum exchange energy is thus a balance between the exchange energy, which favours spin alignment and consequently magnetism, and the kinetic energy, which favours no spin alignment. $E_{\text{promotion}}$ can therefore be written as the sum of the exchange energy and a kinetic energy term [56]:

$$E_{\text{promotion}} = \frac{1}{4} J (T^2 - \mu_i^2).$$  \hfill (7.55)

As before, the cohesive energy is the sum of the bond energy and the repulsive energy. Writing the repulsive energy as

$$E_{\text{rep}_i} = (1 + \mu_i^2) V_i$$  \hfill (7.56)

gives the cohesive energy to be

$$E_{\text{coh}_i} = -\left(\frac{T}{2} - \frac{T^2}{4N}\right) W_i + \mu_i^2 \frac{W_i}{4N} + \frac{1}{4} J (T^2 - \mu_i^2) + \left(1 + \mu_i^2\right) V_i$$

$$= V_i - \left(\frac{T}{2} - \frac{T^2}{4N}\right) W_i + \mu_i^2 \left(\frac{W_i}{4N} + V_i - \frac{J}{4}\right) + \frac{1}{4} J T^2.$$  \hfill (7.57)

The magnetisation state of the system is that which minimises the cohesive energy. Differentiating with respect to $\mu_i$ and equating to zero will always give only one turning point. This turning point always occurs at $\mu_i = 0$. If the coefficient of the $\mu_i^2$ term in equation 7.57 is positive then this turning point is a minimum and so $\mu_i = 0$ minimises the cohesive energy. The system is then paramagnetic. If however the coefficient of $\mu_i^2$ is negative, the turning point is a maximum and it is energetically unstable. The cohesive energy may therefore be lowered by increasing or decreasing $\mu_i$. In this case the minimum energy will be for the states which have the largest, or smallest, possible values of $\mu_i$. See figure 7.7. The maximum magnetisation is
Figure 7.7: Schematic variation of energy with the magnetisation $\mu_i$ with a positive coefficient of $\mu_i^2$ (left) and with a negative coefficient (right). Values of $\mu_i$, outside of the interval $[-\mu_{\text{max}}, \mu_{\text{max}}]$ are unobtainable. The optimum values of $\mu_i$, denoted by the filled circles, are zero and $|\mu_{\text{max}}|$ in the left and right hand cases respectively.

governed by the total number of electrons in the simulation. If the system can hold a maximum of $2N$ electrons split equally between the two bands, then the maximum possible values of $\mu_i$ are:

$$\mu_{\text{max}} = \begin{cases} T, & \text{if } T \leq N \\ 2N - T, & \text{if } N < T \leq 2N \end{cases} \quad (7.58)$$

As the bands are symmetric, the minimum values of $\mu_i$ are simple $-\mu_{\text{max}}$.

### 7.10 Parametrisation

The magnetic two-band model may be parametrised in a similar manner to the s-d band version of the model. There will however be fewer parameters since the two bands have the same width and the repulsions between pairs of each type of band are also the same. The model should require only 5 different parameters as opposed to the 7 used previously, see table 7.1. The exchange parameter $J$ needs to be assigned an appropriate value from experimental data. The parameters $C$, $A$ and $d$ are all free to be chosen so that the potential has the correct form. It is envisaged however that the hopping integral range, $d$ will be similar to the larger value chosen previously; that is, somewhere between the second and third nearest neighbours of the equilibrium fcc phase.
7.11. Summary

In this chapter we have developed a relatively simple many-body potential which is capable of describing the transition of electrons from s-type bands to d-type bands as pressure is applied to the system. Although in computational terms the function is not much more expensive to evaluate than the well proven Finnis-Sinclair type potentials, it is perhaps more awkward to determine good values for the parameters due to the increase in their number. Our potential for caesium was ultimately made by using a combination of computer programs employing either a conjugate-gradients minimisation or a least-squares fitting routine, some manual re-scaling and lots of patience. Unfortunately, there was to fully test the parametrised potential. Initial tests in Monte-Carlo lattice-switch calculations by J. Magee demonstrated that there are two stable fcc phases with different volumes. However, in the time available, he was unable to accurately determine the co-existent volume of the two phases nor the transition pressure.

The two-band model as presented here does not describe the long range Friedel oscillations. Many of the other simple models of particle interactions, such as the Finnis-Sinclair potentials ignore these oscillations with great success. Having said that, it may well be worth adding such a long range tail, since we (see section 6.1.3), and others [93] have shown that the variation of $c/a$ in the hcp phases of barium may be roughly described using only a damped cosine function fitted to the wiggly potential of Hafner and Heine [28], and ignoring the transition of electrons from s-type to d-type orbitals. If such a long range tail was added, the potential may give an excellent description of the various phases in barium as it would combine the two essential ingredients; the transition of electrons from s-type to d-type orbitals and the long range Friedel oscillations. This would then allow a much more detailed study of the bulk properties of the hotel structure. In order to fit the potential to barium however, careful thought would have to be given to the experimental data chosen for use in the fitting procedure.

The magnetic version of the two-band model could, with an appropriate parametrisation, give a good description of the phases of iron. If so, this potential could be of use in modelling the earth’s core and hence in understanding the inner workings of the earth. At core pressures iron is no longer ferromagnetic. However, it is still paramagnetic and so a well parametrised two-band model would be an improvement over the existing one-band models.
Chapter 8

Concluding Remarks

In this thesis, the now well proven *ab initio* programs VASP and CASTEP have been used extensively to study the various phases of the pure elements: barium, bismuth, antimony and, to a much lesser extent, arsenic. In all cases, good general agreement is found between our results and experiment.

For the low pressure bcc phase in barium we have calculated the phonon dispersion curves and the zero-point energies. The dynamical matrix was determined by calculating the forces due to finite displacements of the atoms according to the Hellmann-Feynman theorem. The resulting phonon dispersion curves are in good agreement with those presented elsewhere. Further studies could include calculating these curves at higher pressure and hence evaluating the Gibbs free energy as a function of pressure, as well as determining the phonon density of states and dispersion curves for the hcp and hotel structures. The latter may however have to be postponed until the perturbation theory methods become available.

We have shown that if it were not for the intervention of the hotel structure, the first hcp phase, phase II, would transform smoothly into the second hcp phase, phase V. Although the ultra-soft potential provides a good description of the ratio of $c/a$, the new PAW potential does better. The improvements due to the use of a PAW potential may also extend to the description of the hotel phase and hence the relative stabilities of the two structures.

The ultra-soft potentials gave an acceptable description of the hotel structure not only in barium
but also in bismuth. The bismuth hotel was found to be stable. However, an elastic correction to the energy of the barium hotel was required before it appeared as one of the stable phases. One reason for this is that the ratio $c_{\text{host}}/c_{\text{guest}}$ of the pseudo bismuth hotel was significantly closer to the experimental value than that of the pseudo barium hotel. Also, we demonstrated that the barium hotel is quite similar in bond lengths and electron type to the hcp structure. The energies of the two structures are also very similar. We have not calculated the properties of a bismuth hcp structure, although it would be interesting to do so as they may be very close to the properties of the pseudo bismuth hotel.

As well as studying the high pressure hotel phase of bismuth, we have also studied its other phases; rhombohedral, monoclinic and bcc. Although not much attention was paid to the latter two other than to calculate their energy volume curves, a lot of time was spent studying the rhombohedral phase.

Rhombohedral structures in both bismuth and antimony have been studied. In both cases we find good agreement between the variations with increasing pressure of our calculated cell angle and internal parameter and the variations seen experimentally. There is some debate over whether there is a rhombohedral to simple-cubic transition in antimony and arsenic. The simple-cubic structure is in fact a special case of the rhombohedral structure. Consequently our calculations at, or rather just below, 0 Kelvin exhibit a second-order transition between the two and not a first-order transition as seen experimentally by some groups. Other groups however have not found a first-order rhombohedral to simple-cubic transition. The occasional appearance may be due to the application of the appropriate non-hydrostatic pressure. As mentioned, our calculations exclude the effect of temperature. In order to investigate the effect of temperature we proposed a Landau model of the rhombohedral structure as a distortion of the simple-cubic structure. This model predicted the pressure of the transition from rhombohedral to simple cubic to be lower at higher temperatures. It also predicted a transition at ambient pressure but at a very high temperature. In the case of bismuth, the transition temperature was significantly higher than the melting point. In antimony however, the transition temperature is lower by almost 200 K than the melting point, so a high temperature rhombohedral to simple-cubic transition may be expected. All transitions predicted by the Landau theory however are second-order in nature.
In order to try to verify the prediction of a high temperature transition, we have done some molecular dynamics calculations. Initial results suggest that there could be such a transition. A better approach might be to compare the free energies of the simple-cubic structure with that of the rhombohedral structure. Calculations of the phonon dispersion curves indicate, as would be expected, that the simple-cubic structure is unstable with respect to the R point, \((\frac{1}{2}, \frac{1}{2}, \frac{1}{2})\), phonon mode. The free energy of the simple-cubic structure should therefore be calculated in the quasi-harmonic approach of Drummond and Ackland. Although we have done the requisite phonon calculation for the simple-cubic structure, the calculation has not yet been done for the rhombohedral structure. This approach may yield a first-order transition.

As well as doing \textit{ab initio} calculations, we have also developed an empirical many-body potential, which is capable of modelling the transfer of electrons from one band to another with the application of pressure. We have applied the model to the study of caesium. As the pressure is increased, the electrons are transferred from s-type bands to d-type bands. This ultimately results in the appearance of an iso-structural fcc \(\rightarrow\) fcc transition. The model can also be reformulated in order to model magnetic materials. As yet we have not found values for the various parameters, though we do have a completed potential for caesium. A potential capable of modelling magnetic behaviour should be able to provide a good description of the full character of iron. Currently the only way to treat magnetism is with expensive \textit{ab initio} calculations which significantly limit the size of the magnetic systems which can be investigated. Our simple many-body potential which could enable the study of much larger magnetic systems, would therefore be very useful. One possible application would be to the study of the earth’s interior. Whilst iron is no longer ferromagnetic at the pressures found inside the earth, it is paramagnetic. The two-band model could therefore prove very useful.
Appendix A

The rhombohedral cell

The shape of the rhombohedral cell is generally described by one of three parameters plus either
a length or a volume. The parameters commonly used are the rhombohedral angle, the shear
and the c/a ratio of the cell. Unlike the other two, the latter assumes a specific representation
of the basis vectors.

The rhombohedral angle $\alpha$ and the shear $\varepsilon$ are related as follows [62];

$$\cos \alpha = \frac{1 + 2\varepsilon}{2 + \varepsilon^2}.$$  \hspace{1cm} (A.1)

The c/a ratio is related to the rhombohedral angle by [62]

$$c/a = \sqrt{3} \frac{\cos \rho}{\sin \rho}, \quad \text{where} \quad \sin \rho = \frac{2}{3} \sin \left(\frac{\alpha}{2}\right).$$  \hspace{1cm} (A.2)

The basis vectors may be expressed in terms of the rhombohedral angle with respect to cartesian
axes:

$$\mathbf{b}_1 = a (1, 0, 0)$$ \hspace{1cm} (A.3)

$$\mathbf{b}_2 = a (\cos \alpha, \sin \alpha, 0)$$ \hspace{1cm} (A.4)

$$\mathbf{b}_3 = a \left( \cos \alpha, \frac{1}{\sin \alpha} \left( \cos \alpha - \cos^2 \alpha \right), \sqrt{1 - \frac{2(1 - \cos \alpha)}{\tan^2 \alpha}} \right).$$ \hspace{1cm} (A.5)

Rotating these vectors so that $\mathbf{b}_1 + \mathbf{b}_2 + \mathbf{b}_3$ is parallel to $(1, 1, 1)$ results in a set of basis vectors
which are the cyclic permutations of three numbers. The required rotation is about the axis in
the direction of the vector given by \((b_1 + b_2 + b_3) \wedge (1, 1, 1)\) and is through an angle \(\beta\) given by

\[
\cos \beta = \frac{(b_1 + b_2 + b_3) \cdot (1, 1, 1)}{\sqrt{3} |b_1 + b_2 + b_3|}.
\] (A.6)

Needs \textit{et al.} [62] and others describe the cell with respect to an hexagonal based prism. Their \(c\) axis is chosen to be along \((1, 1, 1)\) and their length \(a\) is the side length of the hexagonal base. This is different to the \(a\) in the rhombohedral description. To avoid confusion, the lengths used in the hexagonal description will be denoted as \(a'\) and \(c'\). The basis vectors are

\[
b'_1 = a \left( \frac{a'}{\sqrt{3}}, 0, \frac{c'}{3} \right)
\] (A.7)

\[
b'_2 = a \left( -\frac{a'}{2\sqrt{3}}, \frac{a'}{2}, \frac{c'}{3} \right)
\] (A.8)

\[
b'_3 = a \left( -\frac{a'}{2\sqrt{3}}, -\frac{a'}{2}, \frac{c'}{3} \right)
\] (A.9)

Note: the order of the vectors has been changed compared with reference [62] so that the volume of the cell is positive. The lengths \(a\), \(a'\) and \(c'\) are related by

\[
a = \sqrt{\frac{a'^2}{3} + \frac{c'^2}{9}}.
\] (A.10)

The primed and unprimed basis vectors are related by a double rotation. The first rotation maps \(b_1 + b_2 + b_3\) onto the \(z\) \((c')\) axis, while the second rotation is about this axis. In the special case that the rhombohedral angle is 60°, the second rotation is through an angle of -90°.
Appendix B

Forces in the two band model

If $E_{coh}$ is the total cohesive energy of the system, the force on the $i^{th}$ atom is given quite generally by,

$$ f_i = -\frac{dE_{coh}}{d\mathbf{r}_i}. $$

(B.1)

In the two band model the cohesive energy is not only a function of the positions of the atoms but also of the electron distribution on each atom $\eta_i$. The force on the $i^{th}$ atom may therefore be written:

$$ f_i = -\sum_j \left( \frac{\partial E_{coh,j}}{\partial \mathbf{r}_i} \bigg|_{\eta_j} + \frac{\partial E_{coh,j}}{\partial \eta_j} \frac{\partial \eta_j}{\partial \mathbf{r}_i} \right). $$

(B.2)

Since the cohesive energy is variational with respect to the electron distribution $\eta_j$, the derivative of the energy with respect to the electron distribution is zero and so the force may be written as

$$ f_i = -\sum_j \frac{\partial E_{coh,j}}{\partial \mathbf{r}_i} \bigg|_{\eta_j}. $$

(B.3)

This is analogous to the Hellmann-Feynman theorem [21] for the \textit{ab initio} calculations, which says that the derivative of the energy with respect to the wave functions is zero, see section 2.14.1. From equations 7.14, 7.15 and 7.17, the cohesive energy in terms of the number of electrons in each band ($n_{i1}$ and $n_{i2}$) is

$$ E_{coh} = \sum_j \left[ \frac{n_{j1}}{2} \left( \frac{n_{j1}}{N_1} - 1 \right) W_{j1} + \frac{n_{j2}}{2} \left( \frac{n_{j2}}{N_2} - 1 \right) W_{j2} + n_{j1} E_{rep,j1} + n_{j2} E_{rep,j2} + n_{j2} E_0 \right], $$

(B.4)
and the force on atom \( i \) is thus

\[
f_i = - \sum_j \left[ \frac{n_{j1}}{2} \left( \frac{n_{j1}}{N_1} - 1 \right) \frac{\partial W_{j1}}{\partial r_i} + \frac{n_{j2}}{2} \left( \frac{n_{j2}}{N_2} - 1 \right) \frac{\partial W_{j2}}{\partial r_i} + n_{j1} \frac{\partial}{\partial r_i} E_{repj1} + n_{j2} \frac{\partial}{\partial r_i} E_{repj2} \right].
\]

From equation \( 7.23 \), the width of band \( b \) on atom \( i \) is \( W_{jb} = \sqrt{\sum_{k \neq j} V_b(r_{jk})} \) and its derivative is

\[
\frac{\partial W_{jb}}{\partial r_i} = \frac{1}{2W_{jb}} \sum_{k \neq j} \frac{\partial}{\partial r_i} V_b(r_{jk}) = \begin{cases} \frac{1}{2W_{jb}} \sum_{k \neq j} \frac{\partial}{\partial r_i} \phi_b(r_{jk}), & \text{if } j = i \\ \frac{1}{2W_{jb}} \frac{\partial}{\partial r_i} \phi_b(r_{jk}), & \text{if } j \neq i. \end{cases}
\]

The repulsive terms are \( E_{repjb} = \sum_{k \neq j} V_b(r_{jk}) \) and their derivatives are

\[
\frac{\partial}{\partial r_i} (E_{repjb}) = \begin{cases} \sum_{k \neq j} \frac{\partial}{\partial r_i} V_b(r_{jk}), & \text{if } j = i \\ \frac{\partial}{\partial r_i} V_b(r_{jk}), & \text{if } j \neq i. \end{cases}
\]

On combining the above equations, the force may then be written:

\[
f_i = - \sum_j \left[ \frac{n_{j1}}{4W_{j1}} \left( \frac{n_{j1}}{N_1} - 1 \right) \frac{\partial \phi_1(r_{ji})}{\partial r_i} + \frac{n_{j2}}{4W_{j2}} \left( \frac{n_{j2}}{N_2} - 1 \right) \frac{\partial \phi_2(r_{ji})}{\partial r_i} \\ + n_{j1} \frac{\partial V_1(r_{ji})}{\partial r_i} + n_{j2} \frac{\partial V_2(r_{ji})}{\partial r_i} \right] \\ - \left[ \frac{n_{i1}}{4W_{i1}} \left( \frac{n_{i1}}{N_1} - 1 \right) \sum_{k \neq i} \frac{\partial \phi_1(r_{ik})}{\partial r_i} + \frac{n_{i2}}{4W_{i2}} \left( \frac{n_{i2}}{N_2} - 1 \right) \sum_{k \neq i} \frac{\partial \phi_2(r_{ik})}{\partial r_i} \\ + n_{i1} \sum_{k \neq i} \frac{\partial V_1(r_{ik})}{\partial r_i} + n_{i2} \sum_{k \neq i} \frac{\partial V_2(r_{ik})}{\partial r_i} \right].
\]

To simplify the appearance of this equation we define

\[
\Omega_{ib} = \frac{n_{ib}(n_{ib} - N_b)}{4N_b W_{ib}}
\]

and the force becomes

\[
f_i = - \sum_j \left[ \Omega_{j1} \frac{\partial \phi_1(r_{ji})}{\partial r_i} + \Omega_{j2} \frac{\partial \phi_2(r_{ji})}{\partial r_i} + n_{j1} \frac{\partial V_1(r_{ji})}{\partial r_i} + n_{j2} \frac{\partial V_2(r_{ji})}{\partial r_i} \right] \\ - \sum_{k \neq i} \left[ \Omega_{k1} \frac{\partial \phi_1(r_{ik})}{\partial r_i} + \Omega_{k2} \frac{\partial \phi_2(r_{ik})}{\partial r_i} + n_{k1} \frac{\partial V_1(r_{ik})}{\partial r_i} + n_{k2} \frac{\partial V_2(r_{ik})}{\partial r_i} \right].
\]
The summations in the second set of square brackets may be reindexed in terms of $j$’s and
included in the first set of square brackets to give

$$
f_i = -\sum_{j \neq i} \left[ \Omega_{i1} \frac{\partial \phi_1(r_{ji})}{\partial r_i} + \Omega_{i2} \frac{\partial \phi_2(r_{ji})}{\partial r_i} + n_{j1} \frac{\partial V_1(r_{ji})}{\partial r_i} + n_{j2} \frac{\partial V_2(r_{ji})}{\partial r_i} + \Omega_{j1} \frac{\partial \phi_1(r_{ij})}{\partial r_i} + \Omega_{j2} \frac{\partial \phi_2(r_{ij})}{\partial r_i} + n_{j1} \frac{\partial V_1(r_{ij})}{\partial r_i} + n_{j2} \frac{\partial V_2(r_{ij})}{\partial r_i} \right]. \tag{B.11}$$

Since both $\phi$ and $V$ are pair potentials $\phi_b(r_{ij}) = \phi_b(r_{ji})$ and $V_b(r_{ij}) = V_b(r_{ji})$. The derivatives of $\phi$ are

$$\frac{\partial}{\partial r_i} \phi_b(r_{ij}) = \frac{\partial}{\partial r_i} \phi_b(r_{ij}) \hat{r}_{ij} = \phi'_b(r_{ij}) \hat{r}_{ij}$$

and

$$\frac{\partial}{\partial r_i} \phi_b(r_{ji}) = \frac{\partial}{\partial r_i} \phi_b(r_{ji}) \hat{r}_{ij} = \phi'_b(r_{ji}) \hat{r}_{ij}$$

where the $\phi'_b$ are scalar quantities and $\phi'_b(r_{ij}) = \phi'_b(r_{ji})$. Similarly, the derivatives of $V$ are

$$\frac{\partial}{\partial r_i} V_b(r_{ij}) = \frac{\partial}{\partial r_i} V_b(r_{ij}) \hat{r}_{ij} = V'_b(r_{ij}) \hat{r}_{ij}$$

and

$$\frac{\partial}{\partial r_i} V_b(r_{ji}) = \frac{\partial}{\partial r_i} V_b(r_{ji}) \hat{r}_{ij} = V'_b(r_{ji}) \hat{r}_{ij}$$

where again the $V'_b$ are scalar quantities.

Finally, the force on atom $i$ is then

$$f_i = -\sum_{j \neq i} \left[ (\Omega_{i1} + \Omega_{j1}) \phi'_1(r_{ij}) + (\Omega_{i2} + \Omega_{j2}) \phi'_2(r_{ij}) + (n_{i1} + n_{j1}) V'_1(r_{ji}) + (n_{i2} + n_{j2}) V'_2(r_{ji}) \right] \hat{r}_{ji} \tag{B.12}$$

with

$$\Omega_{ib} = \frac{n_{ib}(n_{ib} - N_b)}{4N_bW_{ib}}. \tag{B.13}$$
Bibliography


[34] V. Heine. European collaboration in ab-initio computer simulation. *Ψk Newsletter*, 50, April 2002.


[61] Minimisation routines of the numerical algorithms group (nag).


My heart’s in the Highlands, my heart is not here,
My heart’s in the Highlands, a-chasing the deer;
Chasing the wild-deer, and following the roe -
My heart’s in the Highlands, wherever I go!

‘My Heart’s In The Highlands’
Rabbie Burns