

# Atomistic modelling of iron with magnetic analytic Bond-Order Potentials

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# Abstract

The development of interatomic potentials for magnetic transition metals, and particularly for iron, is difficult, yet it is also necessary for large-scale atomistic simulations of industrially important iron and steel alloys. The magnetism of iron is especially important as it is responsible for many of the element's unique physical properties – its bcc ground state structure, its high-temperature phase transitions, and the mobility of its self-interstitial atom (SIA) defects. Yet an accurate description of itinerant magnetism within a real-space formalism is particularly challenging and existing interatomic potentials based on the Embedded Atom Method are suited only for studies of near-equilibrium ferritic iron, due to their restricted functional forms.

For this work, the magnetic analytic Bond-Order Potential (BOP) method has been implemented in full to test the convergence properties in both collinear and non-collinear magnetic iron. The known problems with negative densities of states (DOS) are addressed by assessing various possible definitions for the bandwidth and by including the damping factors adapted from the Kernel Polynomial Method. A 9-moment approximation is found to be sufficient to reproduce the major structural energy differences observed in Density Functional Theory (DFT) and Tight Binding (TB) reference calculations, as well as the volume dependence of the atomic magnetic moments. The Bain path connecting bcc and fcc structures and the formation energy of mono- and divacancies are also described well at this level of approximation. Other quantities such as the high-spin/low-spin transition in fcc iron, the bcc elastic constants and the SIA formation energies converge more slowly towards the TB reference data. The theory of non-collinear magnetism within analytic BOP is extended as required for a practical implementation. The spin-rotational behaviour of the energy is shown to converge more slowly than the collinear bulk energy differences, and there are specific problems at low angles of rotation where the magnitude of the magnetic moment depends sensitively on the detailed structure of the local DOS. Issues of charge transfer in relation to magnetic defects are discussed, as well as inadequacies in the underlying *d*-electron TB model.

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# Chapter 1

## Introduction

The industrial importance of iron and its alloys cannot be overstated. Since the beginning of the Iron Age over three thousand years ago,<sup>1</sup> through the Industrial Revolution of the 18th century and into our modern age, the ability to manipulate the properties of iron and steel has been key to developing many areas of technology. Yet for most of this history steel production was more an experimental art than science. With the discovery of the laws of thermodynamics, however, and a greater understanding of the chemistry of the periodic table, metallurgists have built up a wealth of practical knowledge currently used in the alloying and processing of steels. Nevertheless, it was not until the 20th century that metallurgists began to develop a microscopic model for the behaviour of metals on the macroscale. The works of Hume-Rothery, Raynor and Cottrell led to an electron theory of metals which justified the observed trends in alloying and physical properties, although the methods remained phenomenological and often approximate.<sup>2-4</sup>

A quantitative theory of metals began with the development of the Density Functional Theory (DFT) of Hohenberg, Kohn and Sham,<sup>5,6</sup> as well as related methods, in the 1960s and 1970s. These *ab initio* methods are based on the principle that the total energy of a system of nuclei and electrons may be written as some functional of the electron density, rather than of the full quantum mechanical wave function description of each particle. The electron density with the lowest energy corresponds to the ground state of

the system and is found as the self-consistent solution to the DFT equations. DFT remains one of the most powerful computational tools available to condensed matter physicists and materials scientists concerned with the structure and bonding of materials. However, due to its computational complexity, DFT is also restricted in its application to systems of hundreds to thousands of atoms and mainly static calculations, or dynamic simulations over short time-scales. Approximations must be developed which allow the length- and time-scales of the underlying electronic structure and the physical processes operating on the microstructural level and macroscale to be bridged. This is, in essence, the goal of what has been called *multiscale materials modelling* – to predict the macroscopic properties of engineering components by sequentially developing a physical description from the level of electrons and nuclei up to the continuum. In so doing, the methods should be able to describe the physical and chemical processes operating at a given length scale while clarifying how they contribute to observable phenomena.

The demand for accurate multiscale methods to simulate metals, and particularly iron, is great. The nuclear fission and fusion industries require accurate predictions of the response of iron and its alloys to the intense levels of irradiation, heat and mechanical deformation to which components are subjected in a reactor vessel.<sup>7,8</sup> Traditional industries have also moved towards the production of better quality and less expensive parts, requiring more complex alloys and microstructures. An understanding of the theory underpinning nanostructured metals,<sup>9</sup> highly alloyed steels<sup>10</sup> and novel deformation mechanisms such as TRIP and TWIP would be very useful.<sup>11</sup> Even Earth scientists have turned to modelling to interpret the results of high-pressure and shockwave experiments with the goal of determining the crystal structure and properties of the Earth's iron core.<sup>12</sup> In fact, the original goal of this research was to understand the role of iron nanoparticle catalysts in the growth of single-walled carbon nanotubes. The general utility of iron and steels is, in part, a result of their diverse phase diagrams, allowing the evolution of many different crystal structures with the appropriate metallurgical techniques. The complexity of the phase diagram of elemental iron, as the base for the steels, is a direct result of the

magnetism of the metal.

Simulating iron in all of the suggested applications requires a model for the interactions between particles on the atomistic scale – an interatomic potential. The potential is an approximation to the DFT description of bonding which can be applied to systems of millions of atoms for long time-scales with current computational resources. With tools such as Molecular Dynamics (MD) and kinetic Monte Carlo (kMC), these interatomic potentials can be used to generate defect structures, properties of dislocations, diffusion paths and coefficients, as well as mechanisms of phase transformations, all of which may be used to interpret mechanical properties and construct phase diagrams. Quantities calculated at this level can feed into microstructural modelling methods which treat the material as a continuum. Currently, however, there is a large gap in complexity between the interatomic potentials used for atomistic simulations and the description of the fundamental electronic structure.

The simple form of the most commonly used interatomic potential, the Embedded Atom Method (EAM),<sup>13,14</sup> leads to a lack of transferability in the models. This means the potentials are valid only for those configurations of atoms which have been included in the fitting procedure, and may lead to incorrect results in other simulations. For iron in particular there is a need to incorporate a model for magnetic interactions in the potential, since it has been shown that magnetism significantly affects the energetic stability of both bulk structures and defects. This is an important, and difficult, topic in materials modelling as emphasised by an international workshop on iron and steels in 2008 which concluded that although ‘there has been substantial progress within the last years in constructing interatomic potentials... a lot of work still needs to be done in this field.’<sup>15</sup> Indeed, modelling iron at all levels of accuracy remains a difficult task. Even state of the art DFT functionals have problems describing iron, which often makes coherent modelling difficult. For example, the relative stability of complex magnetic configurations or defect formation energies are functional-dependent. However, while one needs better functionals and further improvements in *ab initio* DFT, simplified interatomic potentials

are still required to help establish a more intuitive rationalisation of bond formation and structural stability.

The analytic Bond-Order Potential (BOP)<sup>16,17</sup> method of Drautz, Pettifor and coworkers provides a framework for developing interatomic potentials of varying complexity from the underlying electronic structure. At its simplest level, the BOP takes a similar form to the EAM. In this thesis it is demonstrated how the BOP method can be extended and applied to treat both collinear and non-collinear magnetism as is required for simulations of iron far from its ground state structure.

In chapter 2, the challenges facing the development of realistic interatomic potentials for iron are summarised. The peculiarities of iron, in terms of its crystal and electronic structures, are explained in terms of an itinerant theory of magnetism. Existing interatomic potentials are assessed on the basis of whether they can reproduce the known properties of iron, and are found lacking. In chapter 3, the Density Functional and Tight-Binding theories are summarised, which underpin the subsequent discussion of the new interatomic potential, the analytic magnetic Bond-Order Potential. In chapter 4, the existing analytic BOP method as per Ref. [17] is described and extended as required for a practical implementation, including the new positive DOS method of Seiser *et al.*<sup>18</sup> Explicit functional forms are derived for the calculation of atomic forces. The results of the method are compared to DFT and TB for collinear calculations; chapter 5 focuses on bulk structures, while chapter 6 deals with various point and planar defects in bcc iron. In chapter 7, the theory of the collinear BOPs is extended to study non-collinear magnetic structures, and to give numerically exact expressions for the derivatives of the energy. The method is tested with some simple non-collinear structures, including the 2-atom bcc cell and the rotation of a single spin in a 16-atom cell. In chapter 8 I conclude.

## Chapter 2

# Challenges for atomistic models of iron

### 2.1 Experimental properties of iron

Under equilibrium conditions pure iron crystallises in the bcc  $\alpha$  ferrite structure, although, as can be seen from the temperature-pressure phase diagram in Fig. 2.1, iron is also allotropic.<sup>19</sup> With increasing temperature,  $\alpha$  transforms first to the fcc  $\gamma$  austenite phase and then to a second bcc  $\delta$  structure. With increasing pressure, the hcp  $\epsilon$  structure is found. As mentioned in the introduction, it is partially this complexity of the elemental phase diagram which leads to the general utility of iron and steels. However, the ground state crystal structure of iron is anomalous when compared to known trends in the periodic table. Moving across the  $4d$  and  $5d$  transition metal elements from left to right (Fig. 2.2), there is an observed trend in crystal structure going from hcp $\rightarrow$ bcc $\rightarrow$ hcp $\rightarrow$ fcc. Iron, along with manganese and cobalt, bucks this trend.

Iron is a ferromagnetic element with a Curie temperature of 1043K. It exhibits unusual magnetic properties, including a non-integral magnetic moment per atom and a specific heat capacity with a strong linear temperature dependence, as expected from a band magnet. This is, however, combined with typical Curie-Weiss behaviour of the magnetic

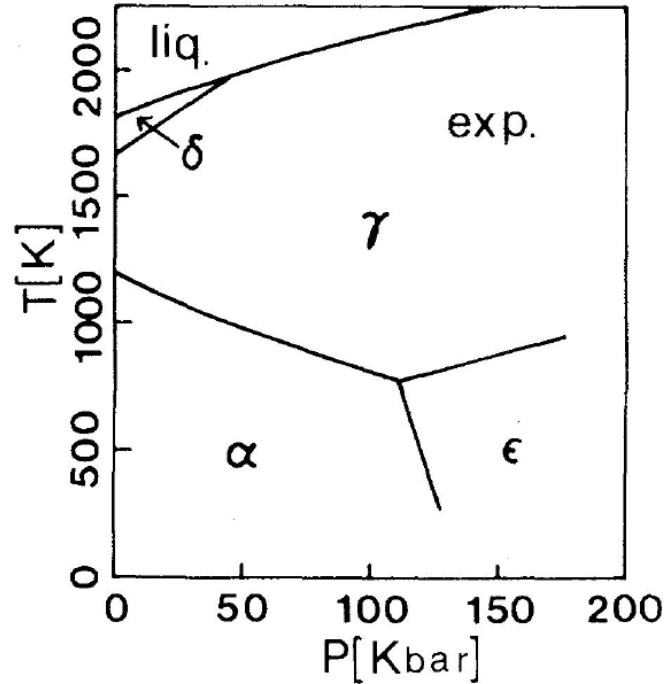


Figure 2.1: The experimental T-P phase diagram of iron<sup>19</sup> showing the bcc  $\alpha$  structure at low temperatures and pressures, the fcc  $\gamma$  structure at intermediate temperatures and the bcc  $\delta$  structure just below the melting point. The hcp  $\epsilon$  structure is observed at higher pressures.

susceptibility at high temperatures consistent with the presence of local magnetic moments. The value of the Curie temperature, at which ferromagnetic ordering disappears, is low if the exchange fields expected in a band model are to be believed.<sup>20,21</sup> This suggests that iron is neither a classical ferromagnet with highly localised magnetic moments nor a completely itinerant magnet. Experimentally, the application of strong magnetic fields is found to shift the transition between  $\alpha$  and  $\gamma$  to higher temperatures.<sup>22</sup> Such magnetic effects may be used to manipulate alloying element solubility<sup>22</sup> and the grain structure of austenitic and carbon steels,<sup>23,24</sup> as well as to stimulate the martensitic phase transformation.<sup>25</sup>

Beyond bulk structures, crystal defects in iron also behave anomalously, particularly the self-interstitial atom (SIA) defects which are known to take up dumbbell structures in bcc metals. While the lowest energy configuration of the dumbbell in the non-magnetic bcc metals lies along the  $\langle 111 \rangle$  crystallographic directions, X-ray scattering experiments

|           |           |           |           |           |           |           |           |           |
|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| <b>Sc</b> | <b>Ti</b> | <b>V</b>  | <b>Cr</b> | <b>Mn</b> | <b>Fe</b> | <b>Co</b> | <b>Ni</b> | <b>Cu</b> |
| hcp       | hcp       | bcc       | bcc       | $\chi$    | bcc       | hcp       | fcc       | fcc       |
| <b>Y</b>  | <b>Zr</b> | <b>Nb</b> | <b>Mo</b> | <b>Tc</b> | <b>Ru</b> | <b>Rh</b> | <b>Pd</b> | <b>Ag</b> |
| hcp       | hcp       | bcc       | bcc       | hcp       | hcp       | fcc       | fcc       | fcc       |
| <b>Lu</b> | <b>Hf</b> | <b>Ta</b> | <b>W</b>  | <b>Re</b> | <b>Os</b> | <b>Ir</b> | <b>Pt</b> | <b>Au</b> |
| hcp       | hcp       | bcc       | bcc       | hcp       | hcp       | fcc       | fcc       | fcc       |

Figure 2.2: The transition metal  $d$  block elements with their ground state crystal structures indicated. The structures of the magnetic elements Mn, Fe and Co can be seen to deviate from the pattern found in the rows below. Mn takes the complex  $\chi$ -phase structure with 58 atoms per unit cell.<sup>26</sup>

show the  $\langle 110 \rangle$  configurations to be lower in energy for iron.<sup>27</sup> Moreover, resistivity experiments show that these SIAs have a particularly high threshold temperature for thermally-activated migration (120K in iron compared to 27K in tungsten, for example).<sup>28</sup>

It is perhaps not surprising that the magnetic  $d$  elements – Mn, Fe, Co – break the trends in non-magnetic crystal structures, and in the next section the direct relationship between structural stability and magnetism will be demonstrated.

## 2.2 Magnetism and structural stability

One indication that magnetism influences structural stability is given by the proximity of the Curie temperature in iron to the  $\alpha \rightarrow \gamma$  transition point. Indeed, magnetism stabilises the bcc ground state, which would otherwise be expected to be hcp in line with the non-magnetic elements of Group VIII, ruthenium and osmium (see Fig. 2.2). This idea is strengthened by the anomalous structures of manganese ( $\chi$ ) and cobalt (hcp), and by the suppression of magnetism in iron associated with the transition to  $\epsilon$  at high pressure.

The trends in the non-magnetic crystal structures have been explained in terms of filling of the electronic  $d$  band. The electronic density of states (DOS) for the transition

metals can be viewed schematically as the overlapping of a broad  $sp$  band with a narrower  $d$  band (see Fig. 2.3). Despite significant  $s$ - $d$  hybridisation in the transition metals (affecting, for example, the cohesive energies of elements such as Ni),<sup>26</sup> it has been shown by Pettifor<sup>29</sup> and Ducastelle and Cyrot-Lackmann<sup>30</sup> that it is the  $d$  electrons which drive the general structural trends. The structure of iron, however, cannot be explained by such a purely electronic effect. The stability of the  $\alpha$  structure can only be explained by magnetic ordering.

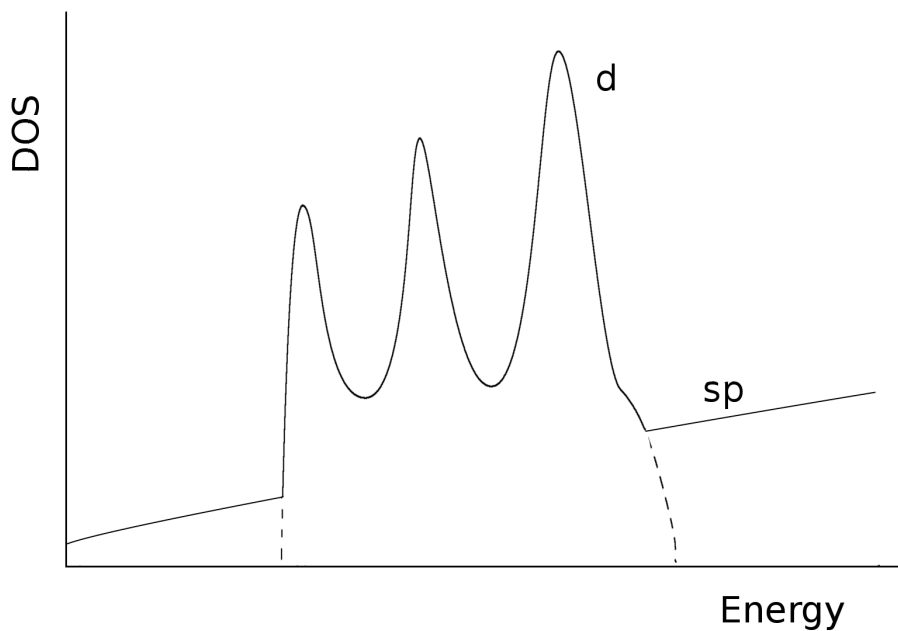


Figure 2.3: Schematic non-magnetic electronic density of states for the transition metal elements, showing a narrow  $d$  band overlapping with a broad  $sp$  band. The particular structure of the  $d$  band DOS dominates the electronic contribution to the structural stability across the transition metal series.

Iron can be described as an *itinerant* magnet which also exhibits local magnetic properties.<sup>31–34</sup> The concept of the local magnetic moment is the easiest to understand and arises most naturally from the free atom case, where the atomic moment is simply the difference in the numbers of spin-up and spin-down electrons in the outer electronic shell. In an insulating solid, where electrons on neighbouring atoms may interact via the process of exchange, the same difference of spin-up and spin-down electrons on each atom defines

a local magnetic moment with an integer value as in the free atom. These moments are, in fact, vector quantities which may be aligned with one another collinearly (as in the commonly known ferromagnetic, antiferromagnetic or ferrimagnetic configurations), or which may take up more exotic non-collinear orientations (either ordered locally in spin spiral structures or disordered and frozen into magnetic glasses).

The distinguishing feature of a metal, however, is that it possesses a *delocalised* electronic structure. The core electron energy levels in the metal are doubly occupied and have no nearby empty states, so do not contribute to the magnetisation. But the electrons near the Fermi surface, at the boundary between empty and filled states, may flip their spins if this becomes energetically favourable. In this case the electronic structure may be divided into two bands, one spin-up and one spin-down channel, with different occupations, leading to a net magnetic moment per atom which may no longer be integer-valued. This is the definition of *band* or *itinerant* magnetism.

The particular combination of the broad *sp* band with a narrow *d* band in the transition metals complicates matters, since the *d* electrons are essentially more tightly bound to the atoms and retain a stronger local character. This combination of localised and delocalised states is at the origin of magnetism in the magnetic transition metals and is the reason why iron exhibits both local and itinerant magnetic properties. The band nature of magnetism in iron was confirmed by the de Haas van-Alphen studies of Gold *et al.*<sup>35,36</sup> in the 1970s. It was shown that the electronic structure in the ferromagnetic state could be decomposed into a superposition of rigidly-shifted non-magnetic bands. The same experiments also showed that the largest contribution to the magnetic shift came from the *d*-like electron states. For this reason, a model for itinerant magnetism of the *d* electrons is sufficient to explain the anomalous crystal structure of iron.

The phenomenological Stoner model<sup>37</sup> has proved particularly useful in explaining specifically low-temperature itinerant ferromagnetism.<sup>32,38,39</sup> As before, it is assumed that the electronic bands may be decomposed into two spin-channels (Fig. 2.4). A magnetic moment is just the difference in occupation of the two channels, with the spin channels

in a non-magnetic material equally filled. A magnetic moment may be produced in an initially non-magnetic structure by transferring electrons near the Fermi level from one channel to another. This process increases the kinetic energy of the electrons as they are forced to occupy higher energy states but reduces the exchange energy since more electrons now have parallel spins. In the Stoner picture this corresponds to a rigid shifting of the bands such that the total Fermi level is constant. If the lowering of the exchange energy is greater than the increase in kinetic energy, the ferromagnetic state will be stabilised.

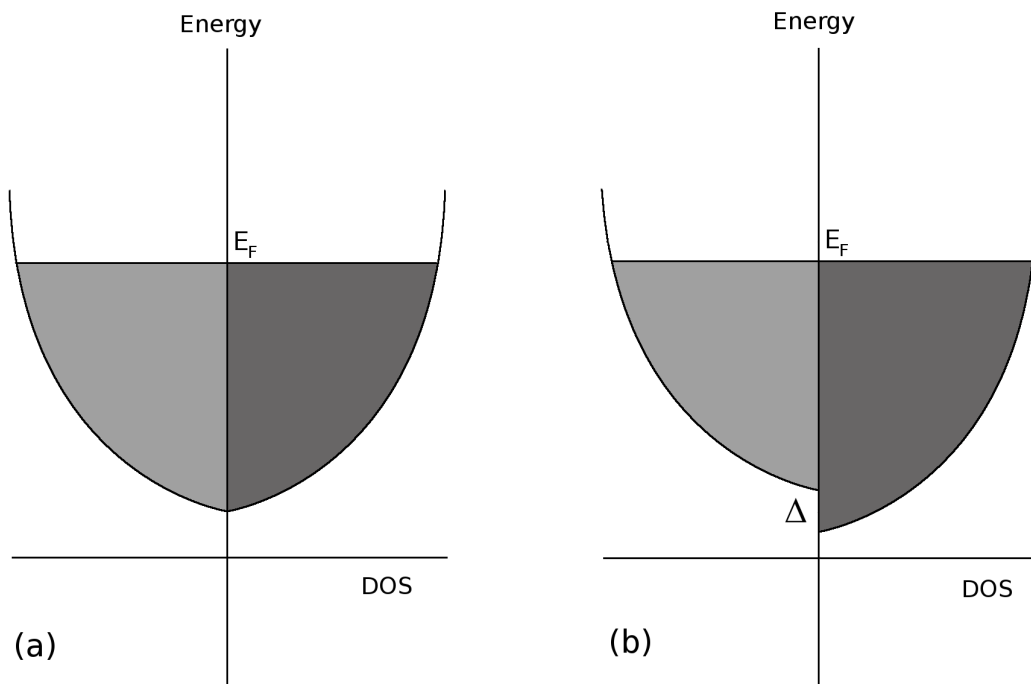


Figure 2.4: Schematic electronic density of states for (a) a non-magnetic metal and (b) a metal with a small ferromagnetic moment per atom. The DOS is decomposed into spin-up and spin-down channels. In (b) the bands have been rigidly shifted by  $\Delta$  to align the Fermi levels in each channel.

The Stoner model may be quantified by assuming to first order that the size of the shift between up- and down-spin bands  $\Delta$ , called the exchange splitting, is proportional to the magnetic moment,

$$\Delta = Im. \quad (2.1)$$

The constant of proportionality,  $I$ , is called the Stoner exchange integral. This assumption is justified by accurate electronic structure calculations which have shown the local

magnetic moment to remain proportional to the exchange field across a wide range of magnetic configurations.<sup>40</sup> It is also consistent with a second-order expansion of the DFT functional as will be seen in section 3.3.4. To generate a moment  $m$  from a non-magnetic DOS,  $\frac{m}{2}$  electrons must be transferred from states just below the Fermi level to states just above. The change in total energy is then the difference between the kinetic and exchange energies. The kinetic energy change on transferring one electron is given by

$$\Delta U_K = \frac{m}{2n(E_F)}, \quad (2.2)$$

while the corresponding change in exchange energy is

$$\Delta U_X = -\frac{Im}{2}, \quad (2.3)$$

where  $n(E_F)$  is the electronic DOS evaluated at the non-magnetic Fermi level. The overall change in energy when  $\frac{m}{2}$  electrons are transferred is given by

$$\Delta U = \Delta U_K + \Delta U_X = \left(\frac{m}{2}\right) \frac{m}{2n(E_F)} - \left(\frac{m}{2}\right) \frac{Im}{2}. \quad (2.4)$$

Simple rearrangement shows that

$$\Delta U = \frac{m^2}{4} \left( \frac{1}{n(E_F)} - I \right), \quad (2.5)$$

which is negative when

$$In(E_F) > 1. \quad (2.6)$$

This is the criterion for the material to exhibit a ferromagnetic instability. If the non-magnetic DOS for a particular structure is high enough at the Fermi level such that criterion (2.6) is satisfied, the crystal will be more stable in a ferromagnetic rather than non-magnetic electronic configuration.

The equilibrium magnetic moment in the spin-polarised state may be determined by

evaluating the average of the non-magnetic density of states between the limits defined by the filled states in the two spin-polarised bands. The change in total energy going from the non-magnetic to the magnetic state is given by the change in band energies and in exchange energy,

$$\Delta U = \int_{E_F}^{E(m)} E n(E) dE - \int_{E(-m)}^{E_F} E n(E) dE - \frac{1}{4} I m^2, \quad (2.7)$$

where  $E(m)$  and  $E(-m)$  are the energies at the limits of band-filling in the majority and minority spin bands,  $n(E)$  is the non-magnetic DOS, and  $E_F$  is the non-magnetic Fermi energy. The magnetic moment is given by

$$m = N^\uparrow - N^\downarrow = 2 \int_{E_F}^{E(m)} n(E) dE, \quad (2.8)$$

which allows for a simple change of variable since

$$\frac{dm}{dE} = 2n(E). \quad (2.9)$$

The change in total energy may then be rewritten as

$$\Delta U = \frac{1}{2} \int_0^m E(m') dm' - \frac{1}{2} \int_{-m}^0 E(m') dm' - \frac{1}{4} I m^2. \quad (2.10)$$

Defining the average density of states as

$$\overline{n(m)} = \frac{m}{E(m) - E(-m)}, \quad (2.11)$$

and exchanging the order of integration leads to the expression

$$\Delta U = \frac{1}{2} \int_0^m \frac{m'}{\overline{n(m')}} dm' - \frac{1}{4} I m^2. \quad (2.12)$$

The ferromagnetic state will be stable when

$$\frac{d\Delta U}{dm} = \frac{m}{2n(m)} - \frac{Im}{2} = 0, \quad (2.13)$$

that is to say when

$$I\overline{n(m)} = 1. \quad (2.14)$$

Eqn. (2.14) defines the stable ferromagnetic moment for a given non-magnetic DOS (as compared to Eqn. (2.6), the criterion for the onset of a magnetic instability). The value of the magnetic moment may be obtained according to

$$m = \frac{E(m) - E(-m)}{I}. \quad (2.15)$$

Since the *sp* band in iron is broad, the structure of the DOS in the vicinity of the Fermi level is dominated by the *d* electrons. Considering Fig. 2.5, a peak is found in the 0K non-magnetic *d* band bcc DOS at the Fermi level. The high DOS value at the Fermi level ensures that the Stoner inequality (2.6) is satisfied and bcc iron is magnetic. The hcp and fcc structures both have lower DOS at the Fermi level. Furthermore, the energy shift due to ferromagnetism is large enough to stabilise the bcc over the hcp structure which is predicted by non-magnetic electronic structure calculations. This phenomenological model does not, however, paint the full picture of magnetism in solids given that many materials exhibit other magnetic configurations as their ground state. A generalised version of the simple Stoner model, as will be shown in chapter 3, may be justified rigorously by a systematic derivation from DFT,<sup>38,41,42</sup> which allows for the energetic separation of the crystal structures with different magnetic ordering to be quantified.

Although useful at 0K, the simple Stoner model is not accurate at elevated temperatures. For example, the Stoner model predicts a very high Curie temperature if the exchange field is taken to be around the expected 1-3 eV.<sup>43</sup> The model only accounts for single particle excitations across the Fermi level, implicit in the inclusion of the Fermi-

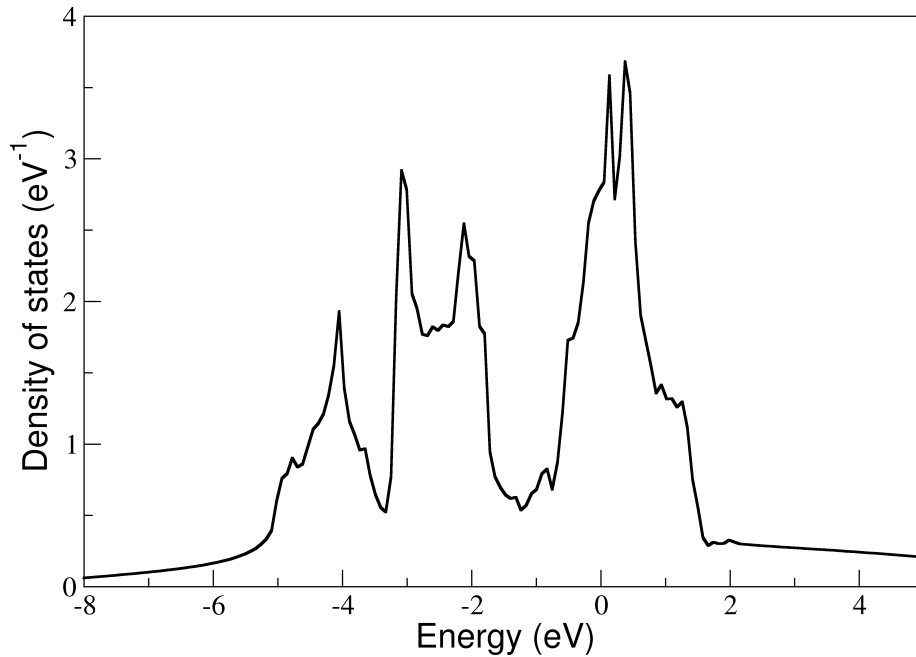


Figure 2.5: Non-magnetic iron bcc DOS calculated with DFT (details of calculation found in chapter 3). The Fermi level is taken as the zero of the energy scale where a large peak is observed in the DOS, satisfying the Stoner criterion for ferromagnetism to be stable in this structure.

Dirac function in the formalism, and so the Stoner transition corresponds to complete collapse of the local exchange fields and thus magnetism. In reality, the magnetic moments tend to disorder with increasing temperature, with  $T_C$  marking the boundary between the ferromagnetic long-ranged order and the high-temperature paramagnetic short-range order. The original Stoner model is unable to account for the temperature-induced non-collinearity needed for an accurate calculation of  $T_C$ . Various competing effects must also be included in the free energy expression at finite temperatures in order to find the structural transitions seen in the Fe phase diagram. These extra terms include the entropic contributions due to the orientational disorder of the magnetic moments as well as their time-dependent fluctuations in magnitude, the collective vibrations of the magnetic structure (spin-waves or magnons) and vibrations of the atomic lattice (phonons), all of

which are temperature-dependent.

The importance of magnetic fluctuations to structural stability was highlighted by experimental work<sup>44</sup> on Fe alloys suggesting two magnetic states were stable in the  $\gamma$  structure – a low-temperature antiferromagnetic state with a small magnetic moment and a high-temperature ferromagnetic state with a moment similar to that in  $\alpha$ . The entropic contribution generated by fluctuations between these two magnetic states was shown to be capable of driving the  $\alpha \rightarrow \gamma \rightarrow \delta$  transitions at zero pressure by Kaufman *et al.*<sup>45</sup> Inden<sup>46</sup> fitted specific heat data for iron, showing that short-range magnetic order in  $\alpha$  existed for a small temperature range above  $T_C$ , which could be linked back to a Stoner model with a locally fluctuating exchange field that had been suggested by Hubbard<sup>43</sup> to justify the use of a Heisenberg-like (i.e. local moments) model at finite temperatures.

Hasegawa<sup>47</sup> concluded that local spin fluctuations must be taken into account within a coherent potential approximation (CPA), where atoms with different magnetic moments are treated analogously to different elements in an alloy model (for which the CPA was originally applied). The CPA allows the density of states to be calculated for a system with a randomly arranged lattice where the perfect periodicity required for standard electronic structure calculations is not present. The environment of each site is replaced by an effective medium generating an averaged potential with which the electron interacts. The CPA is not present in the standard band model and was required in order to reproduce the correct critical behaviour. Pettifor<sup>32</sup> then showed how the coherent potential approximation calculations could be interpreted in a disordered local moments model where individual spins experience an exchange field but equal numbers are allowed to point either up or down such that the averaged field is zero. This simple model was able to explain the trends in magnetic stability across the transition metals (see Fig. 2.6).

This combination of the Stoner theory with a disordered local moments model for finite temperature spin fluctuations within the coherent potential approximation culminated in the first theoretical prediction of the iron phase diagram<sup>48</sup> (Fig. 2.7), showing that the magnetic contributions to the free energy were enough to drive the structural phase

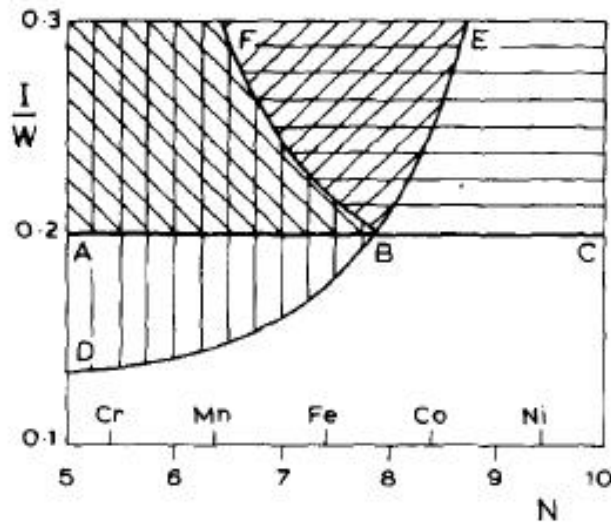


Figure 2.6: A map of the stability regions for ferromagnetic (bounded by FBC) and disordered local moments (bounded by DBF) phases as calculated using a simple Tight Binding model.<sup>32</sup> The ordinate is the dimensionless ratio of the Stoner integral to the width of the electron band. Since the bandwidth decreases as the volume increases, this parameter corresponds to a volume per atom. The abscissa is labelled with the  $d$  band filling. Pure elements are marked at non-integral sites to take into account the effects of  $s$ - $d$  hybridisation.

transitions in iron. The work, however, underestimated the  $\alpha \rightarrow \gamma$  transition temperature because it treated iron as completely disordered above  $T_C$ . The presence of short-range order above  $T_C$  should continue to stabilise the bcc structure to higher temperatures.

These theoretical models allow for an interpretation of the experimental iron phase diagram in terms of magnetic fluctuations. At low temperatures and pressures, the bcc structure is stabilised by ferromagnetism according to the Stoner theory of itinerant magnetism. As the temperature is increased beyond  $T_C$ , the long-range order of the spins is broken but short-range order is maintained. As the temperature is increased further, the point is reached at which the increasing entropic contribution, due to magnetic fluctuations, in the fcc structure brings the fcc free energy below that for the bcc structure, leading to the  $\alpha \rightarrow \gamma$  transition. Eventually the increasing fluctuations in the amplitudes

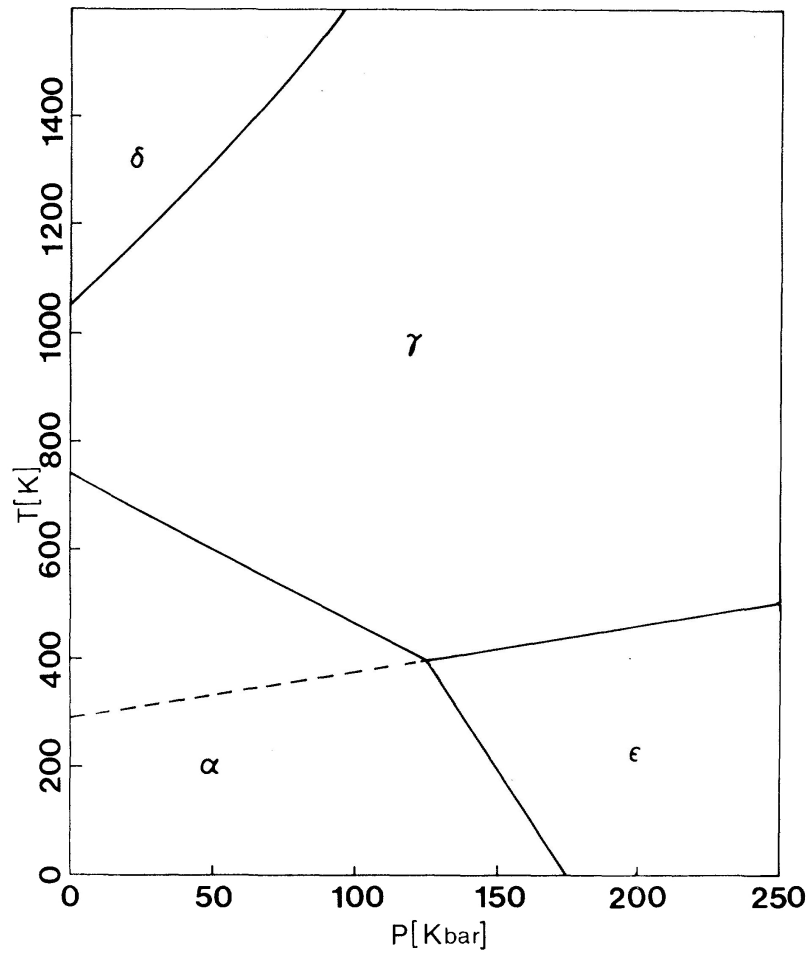


Figure 2.7: The theoretical T-P phase diagram of iron as calculated by Hasegawa and Pettifor<sup>48</sup> using a Stoner-based model extended to high temperatures by the inclusion of a disordered local moments model for spin fluctuations within the coherent potential approximation. The diagram displays the main features seen in the experimental diagram (Fig. 2.1). The liquid phase was not included in the calculations.

of the magnetic moments in the bcc structure restabilise it at the  $\gamma \rightarrow \delta$  transition. Running along the pressure rather than the temperature axis, any increase in pressure causes the electronic bands to widen and the DOS at the Fermi level to drop. This leads to a reduction in the magnetic moments, eventually destabilising the magnetic bcc structure altogether as the Stoner criterion is no longer fulfilled and the  $\alpha \rightarrow \epsilon$  transition occurs.

So far we have neglected the vibrational contributions to the free energy. Recently, Lavrentiev *et al.*<sup>49</sup> have been able to include a model for this vibrational contribution within the Magnetic Cluster Expansion method to study the pure iron phase diagram.

The model allows for local fluctuations in the magnitude and direction of magnetic moments (similar to the single-site fluctuation method of Hasegawa & Pettifor, but extended to include non-collinear magnetic configurations). The interactions between spins are parametrised with DFT data while the vibrational effects are included by fitting a harmonic approximation to experimental data, allowing a quantitative calculation of the structural transition temperatures to within 10%. The Curie temperature of bcc and the Néel temperature of antiferromagnetic fcc are closely reproduced. Lavrentiev *et al.* conclude that both magnetic and vibrational effects are required to reproduce the observed structural transitions within their model, but also that the energy differences involved are on the scale of 1 meV, approaching the theoretical limit of accuracy for DFT.

A further limitation of several of these theoretical methods is their restriction to  $d$  electronic descriptions of the density of states. While the  $d$  electrons alone are sufficient to drive the major structural trends across the transition metal series, as well as explain the ground state magnetisation in bcc Fe, a complete description including  $s$  and  $p$  electrons is required for accurate descriptions of the phonon and magnon behaviour. The precise value of the local magnetic moments depends on the fine structure of the DOS in the vicinity of the Fermi level, which is modified by  $s$ - $d$  hybridisation. In fact, hybridisation between the  $sp$  and  $d$  bands has been shown to stabilise the ferromagnetic configuration of bcc iron over other non-collinear magnetic possibilities.<sup>50</sup>

In summary, while the main driving force for the structural transitions in iron appears to be magnetic in origin, all contributions to the free energy, including temperature-induced non-collinear magnetism and atomic vibrations, are necessary to build a fully quantitative model. High temperature structures of iron and phase transitions, could, therefore, be simulated using computational tools such as Molecular Dynamics (MD) if the underlying interatomic potential were able to model both the basic non-magnetic interactions as well as the contributions due to magnetic fluctuations. So far, such a complete interatomic potential has yet to be constructed.

## 2.3 Current interatomic potentials for iron

### 2.3.1 Non-magnetic potentials

While modern DFT and quantum chemistry methods deal with systems of interacting nuclei and electrons on a fundamental quantum mechanical level, interatomic potentials may be developed to describe systems of atoms interacting with one another through forces derived from a classical description of the energy, written as some analytic function of the atomic coordinates. Although such methods may be derived systematically from more detailed quantum theory, historically they developed quite phenomenologically.

The simplest expression for the energy of a system of nuclei is the pair potential, a model for Coulombic interactions suitable for ionic materials. For metallically bonded atoms, where the electrons are delocalised, the simplest form is found in the Embedded Atom Method (EAM),<sup>13,14</sup> combining a many-body attractive term with a pairwise repulsion,

$$U = \sum_i F(\rho_i) + \frac{1}{2} \sum_{i,j} \Phi(R_{ij}); \quad \rho_i = \sum_j \rho_{atom}(R_{ij}). \quad (2.16)$$

$F$  is the embedding function acting on a local charge density  $\rho_i$  made up from the superposition of spherically-averaged atomic charge densities at each site  $i$ ,  $\rho_{atom}(R_{ij})$ , which themselves are functions of the distance between atom  $i$  and each neighbour  $j$ ,  $R_{ij}$ .  $\Phi$  is a pairwise potential energy function. It is the embedding function which takes account of the unsaturated nature of metallic bonding<sup>26</sup> and whose general form is unknown. For the special case of a Finnis-Sinclair potential,<sup>51</sup> the embedding function takes a square-root form,

$$F_{FS}(\rho_i) = -A\sqrt{\rho_i}. \quad (2.17)$$

The benefit of the EAM is clear; if an appropriate parametrisation can be found for  $F$  and  $\Phi$  then the simple analytic expressions allow the energies and forces to be calculated rapidly, lending themselves to very large-scale MD simulations. Such potentials have found a wide variety of applications and have been used successfully to study many metals.<sup>14</sup>

However, the simplicity of the EAM is also its limitation, as the many-body attractive term is not readily applicable to semiconductors and transition metals where the *directionality* of the bonding is also an important consideration. The expressions also lack any explicit valence-dependence, so models for alloys must be parametrised separately; the mixing of two good elemental models will not necessarily lead to correct alloy results.<sup>16</sup> Furthermore, the simplistic description of the charge density can lead to incorrect charge distributions, and hence forces, around defects in crystals.<sup>52</sup>

Attempts to improve the EAM description of directional bonding have led to the Modified Embedded Atom Method (MEAM),<sup>53,54</sup> where the atomic charge density  $\rho_i$  is written as a sum over angularly-dependent partial charge densities. Directionality is also included in more complex interatomic potentials such as the ‘bond-order potentials’ (to be distinguished from the Bond-Order Potentials extended in this thesis) developed by Abell,<sup>55</sup> Tersoff<sup>56</sup> and Brenner,<sup>57–59</sup> where the angular terms are included inside a many-body ‘bond-order’ combined with pairwise repulsive and attractive potentials.

Various EAM-type potentials have been parametrised for iron. Comparative studies show that they predict different values for most physical properties and so their agreements with both experimental and *ab initio* data vary widely. Becquart *et al.*<sup>7</sup> compared four potentials<sup>51,60–62</sup> for MD simulations of displacement cascades in iron, concluding that ‘the primary damage is very much potential sensitive’. Engin *et al.*<sup>63</sup> investigated whether six potentials<sup>51,64–68</sup> could predict the bcc→fcc structural transition, finding that none of the potentials predicted the correct transition, with the fcc structure metastable at best under conditions when it should be the stable state. Osetsky and Serra,<sup>69</sup> while searching for a potential suitable for modelling the  $\alpha \leftrightarrow \gamma$  reversible transformation, noted that ‘in fact, it is difficult to find a single interatomic potential able to describe the stability of different phases for different temperatures’; they then proceeded to fit a pair potential for this specific transition. The variance in the properties of the EAM potentials is, however, to be expected from the limited analytic form and the lack of transferability resulting from a rigid fit of certain physical properties for the intended application.

### 2.3.2 Magnetic potentials

More recently, a group of EAM-based interatomic potentials has been developed for iron taking into account a simple model for magnetism. Ackland *et al.*<sup>70,71</sup> showed how magnetism could be included within the existing EAM picture without a large increase in complexity, and fitted a potential for use in simulations of the ferritic iron-carbon system. Ackland's two-band model is derived by writing the total energy per atom as a sum of up- and down-spin band energies plus a term due to exchange,

$$U_i = U_i^\uparrow + U_i^\downarrow - E_0 |m_i|^n, \quad (2.18)$$

where  $E_0$  is a constant of proportionality and  $n$  is an integer. Ackland approximates the density of states with the rectangular band model in order to calculate the band energy, which allows a simple conversion to a model of Finnis-Sinclair form in terms of the electron density,

$$U \propto \sum_i \left( -\sqrt{\rho_i} - \frac{1}{\sqrt{\rho_i}} \Theta(2\sqrt{\rho_i} - 5E_0) \right) + \frac{1}{2} \sum_{i,j} \Phi(R_{ij}), \quad (2.19)$$

where  $\Theta$  is the Heaviside step function. When the exchange term is linear in  $m_i$  the model exhibits non-zero magnetisation at all charge densities, while in the quadratic approximation (equivalent to the Stoner model with  $I = E_0$ ) the magnetisation switches from complete to zero at a critical density. Ackland also shows how the enhanced intersite Pauli repulsion between like spins can be incorporated into the pair potential.

Dudarev & Derlet<sup>8</sup> took this method one step further, extending the EAM-type potential for a material with a ferromagnetically-split parabolic DOS, deriving an energy in accordance with the Ginzburg-Landau model for magnetic phase transitions. The Stoner model, over the linear exchange model, is used in the derivation of the magnetic energy contribution since the free-atom energy shows a quadratic dependence on the magnetic moment. Ackland found that the Stoner approximation led to either complete or zero magnetisation within his two-band model, dependent on the density. This problem of

complete magnetisation within Ackland’s theory is, however, attributed to the particular choice of a rectangular DOS which Dudarev & Derlet replace with the parabola. Here this leads to a modification of the embedding functional,  $F$ , (rather than the charge density,  $\rho_i$ , as for the MEAM) such that

$$F_{FS}(\rho_i) = -A\sqrt{\rho_i} - \frac{B}{\ln 2} \left(1 - \sqrt{\frac{\rho_i}{\rho_c}}\right) \ln \left(2 - \frac{\rho_i}{\rho_c}\right) \Theta(\rho_c - \rho_i). \quad (2.20)$$

$\rho_c$  is a critical charge density below which the second ‘magnetic’ term is switched on and above which the embedding functional reverts to the standard Finnis-Sinclair square-root form.

Both of these methods take into account a local volume dependence of the magnetic moments but do not predict structural variations as this would require, within the Stoner picture of magnetism, information about the *shape* of the DOS near the Fermi level. Both sets of potentials are therefore fitted for use in studies of  $\alpha$  iron only. Dudarev & Derlet explicitly developed two sets of fitting parameters, ‘Case I’ and ‘Case II’. While Case I is able to reproduce the correct energetic separation of the non-magnetic and ferromagnetic bcc structures and the ‘magnetic’ fcc structure (whose real lowest-energy magnetic state is, in fact, antiferromagnetic), it does not achieve the correct energetic ordering of the important SIA defects in bcc iron. Case II is refitted for a quantitative agreement between the model and DFT for the SIAs at the expense of the bulk structures. It appears that the EAM method has yet to be extended to describe both the bulk and defect structures simultaneously. This model will be returned to in chapter 5.

A hybrid magnetic/non-magnetic interatomic potential has been developed by Müller *et al.*<sup>72</sup> by mapping the energetic and entropic contributions to the free energy coming from the magnetic fluctuations onto the non-magnetic lattice energies and phonons. This potential takes the form of a modified Tersoff-Brenner analytic bond-order potential, including angular terms adjusted for  $d$  metals, where the energy is written as a sum over

attractive and repulsive Morse potentials multiplied by a many-body ‘bond-order’ term,

$$U = \sum_{i < j} f_{ij}^c(r_{ij}) \left( V_{ij}^R(r_{ij}) - \frac{b_{ij} + b_{ji}}{2} V_{ij}^A(r_{ij}) \right). \quad (2.21)$$

The bond-order is defined as

$$b_{ij} = \frac{1}{\sqrt{1 - \chi_{ij}}}, \quad (2.22)$$

where

$$\chi_{ij} = \sum_{k \neq ij} f_{ik}^c(r_{ik}) g_{ik}(\theta_{ijk}) \exp(2\mu_{ik}(r_{ij} - r_{ik})). \quad (2.23)$$

The key function here is  $g_{ik}(\theta_{ijk})$ . Müller *et al.* use the form derived for *sp*-valent materials, manipulated to fit the observed bonding in *d* elements by adjusting the shape and minimum. An explicit *d*-form of the angular function has, in fact, already been derived.<sup>73</sup>

The Müller potential was used to reproduce the  $\alpha \rightarrow \gamma \rightarrow \delta$  structural trend with increasing temperature by calculating the free energy via thermodynamic integration. The internal energy component of the free energy was adjusted until the correct phase transitions were observed. While the authors show that the potential reproduces the correct energetic ordering of the SIA defects, their analysis of the stability of the bulk bcc and fcc structures seems flawed. Müller *et al.* find that fcc is an energetic minimum with an activation energy barrier separating it from the bcc ground state. This contradicts the accepted behaviour<sup>74</sup> of the energy along the Bain transformation path (where fcc lies at an energetic maximum and is unstable with respect to a transformation to bcc), as well as the DFT results directly quoted in the paper.<sup>75</sup> Moreover, by fitting a non-magnetic model with magnetic data, all information about the local magnetic moments is lost, so it is difficult to interpret the results of any subsequent simulations in terms of experimentally observable physical parameters or magnetic phenomena.

An alternative method, which takes into account the direct relationship between the local crystal structure and the shape of the electronic DOS, is the *numerical* Bond-Order Potential.<sup>76</sup> The BOP is an approximate method for solving the Tight-Binding (TB)

problem, reconstructing the local DOS in terms of its own moments as calculated from elements of the TB Hamiltonian. The relationship between the numerical BOP method and the analytic one described in this thesis will be explained in chapter 3. Mrovec *et al.*<sup>77</sup> have extended the numerical BOP methodology to describe collinear magnetism within the Stoner model and have shown that this provides a good description for the electronic and magnetic structure of iron at 0K. However, the approximate calculation of the DOS in the numerical BOP method leads to an inaccuracy in the Hellmann-Feynman forces<sup>78</sup> such that the energy and forces are inconsistent for low-moment expansions. So far a model for non-collinear magnetism has yet to be included, which would also be required for simulations at finite temperatures.

## 2.4 Summary

The anomalous properties of iron – its crystal structure, temperature-induced phase transformations, and low SIA mobility – can be explained by the magnetic contribution to the total energy which causes a divergence from the property trends expected due to electronic band-filling arguments alone. The phenomenological Stoner model provides an explanation for the ferromagnetic ground state of iron when the electronic DOS is interpreted as a tightly-bound  $d$  band superimposed on a broad, more delocalised  $sp$  band. However, the accurate calculation of other physical properties, such as the phase boundaries used to construct the theoretical phase diagram, requires a more sophisticated model incorporating the free energy contributions of atomic vibrations and non-collinear magnetic orientations induced by temperature and structural disorder, as well as the effects of  $s$ - $d$  or  $sp$ - $d$  hybridisation. The most commonly used interatomic potentials designed for dynamic simulations of metals on the atomistic scale, the EAMs, express the energy as relatively simple functions of the atomic positions and charge densities. These potentials have been extended to model magnetic materials like iron but lack transferability and are only really suitable for simulations of the  $\alpha$  structure. More complex potentials which can

simultaneously treat the details of the electronic and magnetic structure are necessary for simulations of structural transformations at finite temperatures.

## Chapter 3

# Background: Density Functional Theory and the Tight-Binding method

### 3.1 Introduction

Much of the novel work in this thesis will be compared to the results of more fundamental electronic structure methods, especially for properties which are difficult to probe experimentally. The Bond-Order Potentials which are derived later are an approximation to the Tight-Binding method, which itself can be derived rigorously from Density Functional Theory. These two quantum theories have been developed to solve Schrödinger's equation for a system of nuclei and electrons under particular sets of physical constraints. The methods are widely used in materials science and calculations may be performed with a number of free and commercial computational packages. It suffices here to summarise the main features of these methods which are necessary to understand the subsequent chapters as well as to set up the notation which will be used throughout. References to more detailed texts on the theories are provided where relevant.

## 3.2 Density Functional Theory

### 3.2.1 Fundamentals of DFT

For a generic quantum mechanical system made up of  $m$  interacting particles, which in a solid would be the atomic nuclei and electrons, the energy of a particular state of the system is given, neglecting the effects of relativity, by Schrödinger's time-independent equation,

$$\hat{H}\Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_m) = E\Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_m), \quad (3.1)$$

where  $\hat{H}$  is the Hamiltonian operator and  $E$  is the energy of the state with many-body wavefunction  $\Psi$  defined by the set of coordinates of each particle  $\{\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_m\}$ . Assuming the Born-Oppenheimer adiabatic approximation<sup>79</sup> to hold, at any given time the electrons of the system are moving much more quickly than the more massive nuclei and so the kinetic energy operator for the nuclei may be subtracted from  $\hat{H}$ . In this case the Hamiltonian can be written as the sum of the electronic kinetic energy, the Coulomb interaction between the moving electrons and static nuclei, and the Coulomb interaction between electrons. Combined with the antisymmetry of the wavefunction, the Coulomb interaction leads to the correlated motion of the electrons.

The solution to the manybody Schrödinger equation is intractable for all but the simplest of scenarios but the two theorems of Hohenberg and Kohn<sup>5</sup> show how the problem can be rewritten in terms of the electron density,  $n(\mathbf{r}_i)$ , at each point in space. The first theorem proves that the total energy of a system of electrons may be written as a functional of the electron density rather than of the full wavefunction, while the second theorem proves that the ground state electron density minimises this energy functional. The ground state density uniquely defines the external potential.

Although the functional form is in general unknown, Kohn and Sham<sup>6</sup> were able to show that it can be constructed for a system of non-interacting electrons with the same electron density moving under the influence of an effective external potential. The

neglected exchange and correlation (XC) terms missing from the non-interacting system and the differences in electronic kinetic energies between the two systems can be grouped together into an effective XC functional. The energy may then be written as<sup>80</sup>

$$U[n] = T[n] + U_C[n] + U_N[n] + U_{XC}[n], \quad (3.2)$$

where  $T$  is the electronic kinetic energy functional for the non-interacting system,  $U_C$  is the functional for the Coulomb interaction between electrons,  $U_N$  is the functional for the interaction of the electrons with the external potential (generated by the static nuclei), and  $U_{XC}$  is the exchange and correlation functional.  $T$ , along with a non-interacting effective potential  $V$ , defines the energy of the non-interacting system via the Kohn-Sham equations<sup>80</sup>

$$\left[ -\frac{\hbar}{2m} \nabla^2 + V(\mathbf{r}) \right] \psi_n(\mathbf{r}) = \epsilon_n \psi_n(\mathbf{r}), \quad (3.3)$$

where

$$V(\mathbf{r}) = V_C(\mathbf{r}) + V_N(\mathbf{r}) + V_{XC}[n(\mathbf{r})]. \quad (3.4)$$

The electron density of the interacting system can be reproduced from the Kohn-Sham orbitals,

$$n(\mathbf{r}) = \sum_n^{occ} |\psi_n(\mathbf{r})|^2. \quad (3.5)$$

Since the effective potential Eqn. (3.4) depends on the electron density, these sets of equations must be solved iteratively until the self-consistent ground state density is found. The calculation may proceed by expanding the Kohn-Sham orbitals onto whichever basis is most computationally efficient for the problem at hand. For metals the basis most commonly used consists of plane waves (which are eigenstates of the free electron model), although a linear combination of atomic-like orbitals is often more chemically intuitive. Once the ground state charge density is found, the energy of the system is known and other quantities such as the force or stress may be calculated.<sup>80,81</sup>

In general, the variation of the total energy with respect to some parameter  $\Lambda$ , on which

the external potential  $V$  depends, is given by the Hellmann-Feynman Theorem,<sup>78,82</sup>

$$\frac{\partial U}{\partial \Lambda} = \langle \Psi_0 | \frac{\partial V}{\partial \Lambda} | \Psi_0 \rangle, \quad (3.6)$$

where  $\Psi_0$  is the ground state wavefunction. In DFT, this leads to an expression for the force on an atom  $i$ , given by<sup>83</sup>

$$\mathbf{F}_i = -\frac{\partial U[n_0]}{\partial \mathbf{R}_i} = -\int n_0(\mathbf{r}) \frac{\partial V(\mathbf{r})}{\partial \mathbf{R}_i} d\mathbf{r}. \quad (3.7)$$

$\mathbf{R}_i$  is the position vector of atom  $i$  and  $n_0$  is the ground state charge density. Note that the force only depends on the derivative of the potential, and not on the derivative of the charge density itself, since the first order fluctuations vanish. This expression is therefore only valid when the energy has already been minimised with respect to the charge density (or equivalently, when the charge density has been found self-consistently), and small inaccuracies in the charge density can lead to nonsensical forces.<sup>83</sup>

### 3.2.2 Spin DFT

So far we have only considered the electron density as a scalar field. Since the electrons possess a spin which is either up or down, we may define the wavefunction as a  $2 \times 1$  vector, called a spinor,

$$\boldsymbol{\psi}_n = \begin{pmatrix} \psi_{n\uparrow}(\mathbf{r}) \\ \psi_{n\downarrow}(\mathbf{r}) \end{pmatrix}. \quad (3.8)$$

Then the electron density becomes

$$n(\mathbf{r}) = \sum_{n,\nu}^{occ} |\psi_{n\nu}(\mathbf{r})|^2, \quad (3.9)$$

and we may define a new quantity, the  $2 \times 2$  spin density matrix, as

$$\rho_{\nu\nu'}(\mathbf{r}) = \sum_n^{occ} \psi_{n\nu}(\mathbf{r}) \psi_{n\nu'}^*(\mathbf{r}), \quad (3.10)$$

or in matrix form,

$$\boldsymbol{\rho}(\mathbf{r}) = \sum_n^{occ} \boldsymbol{\psi}_n(\mathbf{r}) \times \boldsymbol{\psi}_n^\dagger(\mathbf{r}), \quad (3.11)$$

where  $\psi^*$  and  $\boldsymbol{\psi}^\dagger$  represent the respective complex conjugate and conjugate transpose of the wavefunction. The Density Functional Theory described previously can be rewritten taking the spin density matrix as the central quantity which must be solved for in a self-consistent fashion.<sup>84,85</sup> This allows for the definition of a  $3 \times 1$  magnetisation field whose components along the Cartesian axes may be extracted from the spin density matrix,

$$\mathbf{m}(\mathbf{r}) = \sum_n^{occ} \sum_{\nu\nu'} \psi_{n\nu}(\mathbf{r}) \boldsymbol{\sigma}_{\nu\nu'} \psi_{n\nu'}^*(\mathbf{r}), \quad (3.12)$$

using the vector of Pauli matrices,  $\boldsymbol{\sigma}$ , whose components

$$\boldsymbol{\sigma} = \begin{pmatrix} \boldsymbol{\sigma}_x \\ \boldsymbol{\sigma}_y \\ \boldsymbol{\sigma}_z \end{pmatrix}, \quad (3.13)$$

are defined by

$$\boldsymbol{\sigma}_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}; \quad \boldsymbol{\sigma}_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}; \quad \boldsymbol{\sigma}_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \quad (3.14)$$

The electron density is the trace of the spin density matrix in spin space,

$$n(\mathbf{r}) = \boldsymbol{\rho}_{\uparrow\uparrow}(\mathbf{r}) + \boldsymbol{\rho}_{\downarrow\downarrow}(\mathbf{r}), \quad (3.15)$$

and the magnetisation field can be written as

$$\mathbf{m}(\mathbf{r}) = \begin{pmatrix} m_x(\mathbf{r}) \\ m_y(\mathbf{r}) \\ m_z(\mathbf{r}) \end{pmatrix} = \begin{pmatrix} \rho_{\uparrow\downarrow}(\mathbf{r}) + \rho_{\downarrow\uparrow}(\mathbf{r}) \\ i(\rho_{\downarrow\uparrow}(\mathbf{r}) - \rho_{\uparrow\downarrow}(\mathbf{r})) \\ \rho_{\uparrow\uparrow}(\mathbf{r}) - \rho_{\downarrow\downarrow}(\mathbf{r}) \end{pmatrix}. \quad (3.16)$$

The magnetic moment,  $\mathbf{m}$ , is measured in Bohr magnetons,  $\mu_B$ . The experimentally measurable magnetisation,  $\mathbf{M}$ , defined as the number density of magnetic dipole moments, may be calculated according to

$$\mathbf{M} = \frac{1}{V_{\text{cell}}} \int_{\text{cell}} \mathbf{m}, \quad (3.17)$$

where  $V_{\text{cell}}$  is the volume of the unit cell.

In the most general non-collinear DFT codes a global axis for the spin quantisation is not assumed, which may instead vary from point to point in space. A magnetisation density which varies three-dimensionally in direction from point to point describes the state of non-collinear magnetism where local magnetic moments are not required to remain parallel or antiparallel to one another (as in ferromagnetic, antiferromagnetic and ferrimagnetic structures) but may be canted. The local spin directions may, however, be constrained to lie parallel to a global axis such that collinearity of the magnetic moments is enforced. In this case the off-diagonal elements of the spin density matrix vanish and the Schrödinger equations for the up- and down-spin channels decouple so that they may be solved separately, simplifying the calculation.

The electron and magnetisation densities are continuous fields in real space and are not associated with particular atoms in the crystal. Chemically intuitive quantities such as the charge or magnetic moment on an atom may be approximated from common self-consistent plane wave calculations by partitioning the space around a site. Calculating the spin density within spheres of a given radius around each atom will always underestimate the total charge if neighbouring spheres are allowed just to touch, or attribute spin density

to multiple sites if the spheres are allowed to overlap. Alternatively, the space between nuclei may be partitioned geometrically such that no charge is lost, but the particular topologies of the ‘atoms’ generated will bear little relation to the shapes of free atoms. Atomic charges and magnetic moments may be projected onto localised basis sets such as atomic-like orbitals, although the projection method is never unique.

### 3.2.3 Exchange and correlation

The ultimate accuracy of DFT, assuming a choice of complete basis set and fully-converged calculations, depends on the particular XC functional. The form is known exactly for none but the simplest of cases and various approximations have been developed to treat different systems. The simplest form of the functional is the Local Density Approximation (LDA),<sup>83</sup>

$$U_{XC}^{LDA}[\rho(\mathbf{r})] = \int \rho(\mathbf{r}) \epsilon_{XC}(\rho(\mathbf{r})) d\mathbf{r}, \quad (3.18)$$

where  $\epsilon_{XC}(\rho(\mathbf{r}))$  is the exchange-correlation energy per particle in a homogeneous electron gas with density  $\rho(\mathbf{r})$ . The exchange term in this case can be determined analytically while the correlation is calculable via Monte Carlo methods. The LDA provides a good description for many solids although it has a tendency towards overbinding of materials and it is less successful for systems containing the more strongly correlated  $d$  and  $f$  electrons.<sup>80</sup> An extension is the Generalised Gradient Approximation (GGA) which also takes into account the local gradients of the electron density within certain restrictions. The GGA has been shown to compensate for the LDA’s tendency to over-bind.<sup>86</sup>

Both of these approximations may be extended to spin-polarised calculations. For collinear magnetic calculations the XC potential takes the simple form of a diagonal matrix in spin-space since the up- and down-spin channels are decoupled. In the non-collinear case the XC potential must be a functional of the full spin density matrix although the same analytic expressions may be used as for the collinear case as long as the spin-coordinate space is rotated locally at each point such that the spin density matrix is

diagonalised. In the case of iron, the spin-polarised LDA erroneously favours a non-magnetic hcp structure over the known ferromagnetic bcc ground state. The tendency to pull the atoms closer together results in an underestimation of the magnetisation and hence the magnetic contribution to the energy which should stabilise bcc. The GGA is able to overcome this problem.

### 3.2.4 DFT studies of iron

The major structures of pure iron have been studied in detail with spin-polarised DFT by Herper *et al.* (see Fig. 3.1).<sup>87</sup> As mentioned previously, the spin-polarised LDA ground state of iron is a non-magnetic close-packed structure. The LDA underestimates the contribution of the ferromagnetic energy which must stabilise the bcc structure. This is corrected by the GGA calculations, although compounds or alloys of iron, such as Fe<sub>3</sub>Al, may still be described more accurately within the LDA.<sup>88</sup>

The spin-polarised DFT has also been used to study the energetics of iron phase transitions.<sup>87</sup> Non-collinear DFT has been used to investigate the subtle energy differences between magnetic structures in  $\gamma$  iron, which are found to be spin density waves incommensurate with the atomic lattice rather than the simple  $2\gamma$ -state model discussed in the introductory chapter.<sup>89–91</sup> Such non-collinear structures are believed to be responsible for the anti-Invar effect in fcc iron. DFT also predicts a weakly non-collinear ground state for the pressurised  $\epsilon$  phase up to 50GPa, although so far this has not been confirmed by experiment since the calculated hyperfine fields are too weak for detection with Mössbauer spectroscopy.<sup>89</sup>

### 3.2.5 Computational methodology

Unless otherwise stated, all DFT results shown in this thesis were calculated using the Vienna ab initio simulation package (VASP)<sup>92,93</sup> with the projector-augmented wave (PAW)<sup>94,95</sup> pseudopotential method. The GGA exchange-correlation functional of Perdew,

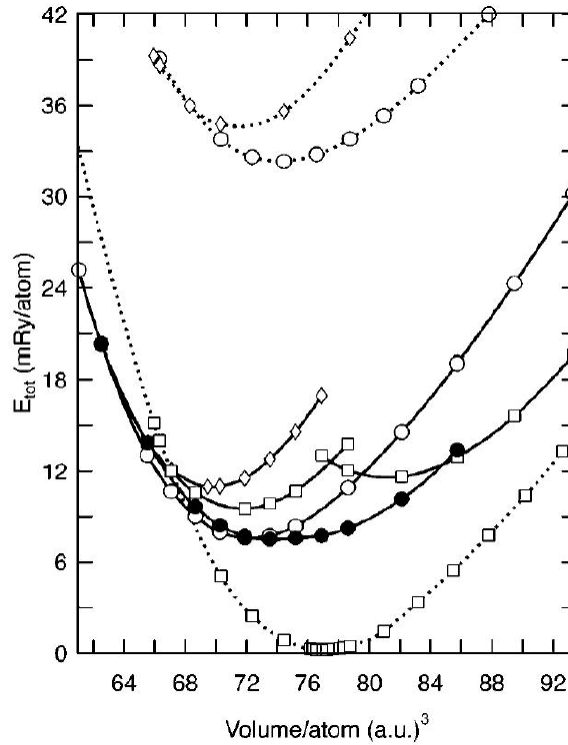


Figure 3.1: The total energies of iron calculated using the GGA by Herper *et al.*<sup>87</sup> The solid curves correspond to fcc and the dashed to bcc. Nonmagnetic structures are diamonds, ferromagnetic structures are squares, and open and filled circles represent two different antiferromagnetic structures. Ferromagnetic bcc is found to be the ground state structure.

Burke and Ernzerhof (PBE)<sup>96</sup> was chosen as it has been shown previously to give accurate results for magnetic iron. Calculations were performed in reciprocal space using a Monkhorst-Pack<sup>97</sup> scheme to sample the Brillouin zone, with subsequent integration being performed using the linear tetrahedron method with Blöchl corrections.<sup>98</sup> The  $k$ -point density was determined so as to achieve a convergence in the total energy of 1 meV/atom. The plane wave basis set was used to expand the electronic wavefunctions up to a cutoff kinetic energy of 350 eV.

### 3.3 Tight-Binding method

#### 3.3.1 Basis sets and the TB secular equation

The underlying assumption behind the orthogonal Tight-Binding (TB) method is that the electrons in a system feel a strong attraction to the nuclei and so spend a significant proportion of their time near one atom rather than travelling through the crystal as is assumed in a free electron model. This approximation is justified for covalently-bonded materials and metals with valence  $d$  electrons. We can therefore assume that the electrons remain in atomic-like orbital states when near a particular atom and are able to hop between these states as they move through the lattice, resulting in the choice of a minimal basis set made up of localised atomic orbitals (the Linear Combination of Atomic Orbitals or LCAO approach) to expand the electronic wavefunction.

Historically, TB developed as a method for interpolating between data points calculated with more accurate theories. Slater & Koster<sup>99</sup> combined Bloch's LCAO concept<sup>100</sup> with an approximate Hamiltonian matrix parametrised with real-space functional forms. Their seminal paper showed how appropriate combinations of relatively simple bond integrals between atoms could be used to interpolate between high-symmetry points in  $k$ -space where more accurate DFT calculations are computationally less taxing. However, the modern TB method is much more powerful than this. By fitting TB models to *ab initio* bandstructures for simple crystal structures they can be used in total energy calculations of much more complex systems containing far more atoms than in the basic unit cell.

The electronic wavefunction is expanded in terms of the set of atomic orbital basis functions,  $\{\phi_{i\alpha}(\mathbf{r} - \mathbf{R}_i - \mathbf{R})\}$ , in accordance with Bloch's Theorem<sup>100</sup> for periodic materials,

$$\psi_{\mathbf{k}}^{(n)}(\mathbf{r}) = \sum_{\mathbf{R}} \sum_{i\alpha} c_{i\alpha}^{(n)}(\mathbf{k}) e^{i\mathbf{k} \cdot \mathbf{R}} \phi_{i\alpha}(\mathbf{r} - \mathbf{R}_i - \mathbf{R}), \quad (3.19)$$

where  $\mathbf{k}$  labels a point in  $k$ -space and  $\mathbf{R}$  is the lattice vector of the crystal. Schrödinger's

equation may then be written in  $k$ -space as

$$\hat{H}\psi_{\mathbf{k}}^{(n)}(\mathbf{r}) = E_{\mathbf{k}}^{(n)}(\mathbf{r})\psi_{\mathbf{k}}^{(n)}(\mathbf{r}). \quad (3.20)$$

Defining the real-space Hamiltonian matrix elements between atom  $i$ , orbital  $\alpha$  and atom  $j$ , orbital  $\beta$  as

$$H_{j\beta i\alpha}(\mathbf{R}_j - \mathbf{R}_i) = \int \phi_{j\beta}^*(\mathbf{r} - \mathbf{R}_j) \hat{H} \phi_{i\alpha}(\mathbf{r} - \mathbf{R}_i) d\mathbf{r}, \quad (3.21)$$

and the overlap matrix elements as

$$S_{j\beta i\alpha}(\mathbf{R}_j - \mathbf{R}_i) = \int \phi_{j\beta}^*(\mathbf{r} - \mathbf{R}_j) \phi_{i\alpha}(\mathbf{r} - \mathbf{R}_i) d\mathbf{r}, \quad (3.22)$$

we may write down their momentum-space equivalents via the Fourier transform,

$$H_{j\beta i\alpha}(\mathbf{k}) = \sum_{\mathbf{R}} H_{j\beta i\alpha}(\mathbf{R}_j - \mathbf{R}_i - \mathbf{R}) e^{i\mathbf{k} \cdot \mathbf{R}}, \quad (3.23)$$

and

$$S_{j\beta i\alpha}(\mathbf{k}) = \sum_{\mathbf{R}} S_{j\beta i\alpha}(\mathbf{R}_j - \mathbf{R}_i - \mathbf{R}) e^{i\mathbf{k} \cdot \mathbf{R}}, \quad (3.24)$$

where  $\mathbf{R}$  is a lattice vector,

$$\mathbf{R} = n_i \mathbf{a}_i; \quad i = 1, 3 \quad (3.25)$$

with  $a_1, a_2$  and  $a_3$  the unit cell vectors. By premultiplying Schrödinger's equation (3.20) by  $\psi_{\mathbf{k}}^{*(n)}(\mathbf{r})$  and expanding the wavefunctions in terms of the localised basis, we arrive at the TB secular equation,

$$\sum_{i\alpha} [H_{j\beta i\alpha}(\mathbf{k}) - E^{(n)}(\mathbf{k}) S_{j\beta i\alpha}(\mathbf{k})] c_{i\alpha}^{(n)}(\mathbf{k}) = 0. \quad (3.26)$$

The solution of the secular equation yields the TB band structure which may be integrated to find the energy for a particular band-filling.

TB models generally involve a further set of approximations for the Hamiltonian and overlap matrices. It is assumed that the important direct interactions between atoms remain local and so we restrict the interaction distances to first, second, or third nearest neighbours by allowing the hopping and overlap integrals to decay to zero by a certain cutoff distance. We neglect three-centre integrals which involve the wavefunctions on two atoms interacting via the potential of a third and in many cases we neglect the overlap integrals entirely, working with orthogonal basis sets only. The diagonal elements of the Hamiltonian, the onsite levels, are approximated as atomic quantities by neglecting their dependence on the presence of other atoms, called the crystal field.

The remaining Hamiltonian integrals are parametrised as simple distance-dependent functions fitted to accurate data, allowing us to ignore the particular functional forms of the orbitals themselves.<sup>83</sup> By rotating the coordinate system such that the  $z$  axis lies along each bond, the matrix elements may be decomposed into a combination of distance-dependent bond integral functions,  $\beta_\lambda(\mathbf{r})$ . For a  $d$  electron system, there are three possible types of bond interaction,  $\lambda$ , between orbitals to be parametrised:  $dd\sigma$ ,  $dd\pi$  and  $dd\delta$ . The tables of Slater & Koster<sup>99</sup> may be used to calculate the Hamiltonian matrix elements, Eqn. (3.21), from a knowledge of the direction cosines of each bond and the particular bond integral parametrisation.

There are various routes to extract TB bond integrals from a full DFT calculation. In one method,<sup>101</sup> for example, a plane-wave DFT bandstructure is projected onto a pseudo atomic orbital basis, where each ‘orbital’ function consists of the product of an angular function with multiple radial functions (this so-called multiple- $\zeta$  basis is required to achieve results numerically consistent with the plane wave calculation). This basis is then itself projected, or ‘downfolded’, onto a minimal basis of atomic orbitals, which may be orthogonalised via the Löwdin transformation.<sup>102</sup> The Hamiltonian matrix elements between orbitals on two sites, rotated into the direction of the bond, are taken as the TB bond integrals.

### 3.3.2 The density matrix and density of states

The density matrix within the TB model may be calculated by the  $k$ -space integration of the expansion coefficients of the eigenvectors found as a solution to the TB secular equation,

$$\rho_{i\alpha j\beta}(\mathbf{R}_i - \mathbf{R}_j - \mathbf{R}) = \sum_n \int_{\text{BZ}} f^{(n)}(\mathbf{k}) c_{j\beta}^{(n)*}(\mathbf{k}) c_{i\alpha}^{(n)}(\mathbf{k}) e^{i\mathbf{k} \cdot \mathbf{R}} d\mathbf{k}, \quad (3.27)$$

where  $f^{(n)}$  determines the occupancy of a particular state  $n$  ( $f^{(n)} = 1$  below the Fermi level and  $f^{(n)} = 0$  above) and  $\int_{\text{BZ}}$  indicates the integral is taken over the first Brillouin Zone. A closely related quantity commonly used in the TB literature is the bond-order matrix defined by

$$\Theta_{i\alpha j\beta} = 2\rho_{i\alpha j\beta}, \quad (3.28)$$

where  $i \neq j$  in the standard definition. The band energy of a structure is given by the product of the density matrix with the Hamiltonian,

$$U_{\text{Band}} = 2\text{Tr}(\rho\mathbf{H}) = 2 \sum_{i\alpha j\beta} \sum_{\mathbf{R}} \rho_{i\alpha j\beta}(\mathbf{R}_i - \mathbf{R}_j - \mathbf{R}) H_{j\beta i\alpha}(\mathbf{R}_j - \mathbf{R}_i - \mathbf{R}), \quad (3.29)$$

where  $\text{Tr}$  indicates the trace of the matrix product, while the bond energy contains only the intersite terms contributing to the band energy,

$$U_{\text{Bond}} = 2 \sum_{i\alpha j\beta, i \neq j} \sum_{\mathbf{R}} \rho_{i\alpha j\beta}(\mathbf{R}_i - \mathbf{R}_j - \mathbf{R}) H_{j\beta i\alpha}(\mathbf{R}_j - \mathbf{R}_i - \mathbf{R}). \quad (3.30)$$

The factor of 2 accounts for spin degeneracy in a non-magnetic system.

An alternative formulation for the TB model makes use of the local density of states function which has already been integrated across  $k$ -space,

$$n_{i\alpha}(E) = \sum_n \left| c_{i\alpha}^{(n)} \right|^2 \delta(E - E_n). \quad (3.31)$$

The band energy may be rewritten as

$$U_{Band} = \sum_{i\alpha} 2 \int^{E_F} E n_{i\alpha}(E) dE, \quad (3.32)$$

and for the bond energy,

$$U_{Bond} = \sum_{i\alpha} 2 \int^{E_F} (E - E_{i\alpha}) n_{i\alpha}(E) dE, \quad (3.33)$$

where  $E_{i\alpha}$  is shorthand for the onsite level  $H_{i\alpha i\alpha}$ .

### 3.3.3 TB bond model

Within the TB *bond* model<sup>103</sup> for a  $d$ -valent elemental system in particular, the binding energy is written as the sum of the bond energy and a pairwise repulsive term,

$$U_B = U_{Bond} + U_{Rep}. \quad (3.34)$$

The bond energy is chosen over the band energy to maintain consistency with the force theorem<sup>104,105</sup> which states that there must be no force contribution from the self-consistent redistribution of charge due to the virtual displacement of an atom, which is violated by the non-self-consistent band model. The bond model satisfies the force theorem when the onsite levels are calculated self-consistently. In the original method the onsite levels are shifted iteratively to achieve a state of Local Charge Neutrality (LCN), a reasonable assumption for metals where electrons are shared equally between atoms. LCN is not the only possible self-consistent solution and terms may be added to the Hamiltonian to control the amount of self-consistent charge transfer between sites. Once the charges are calculated self-consistently, one may work with either the bond or the band energy. The papers of Sutton *et al.*<sup>103</sup> and Foulkes & Haydock<sup>106</sup> show how the TB bond model may be derived systematically from DFT. The Hellmann-Feynman Theorem<sup>78,82</sup> force on an

atom  $l$  derived from the bond energy,

$$\mathbf{F}_l^{Bond} = \sum_{i\alpha j\beta, i \neq j} \Theta_{i\alpha j\beta} \nabla_l H_{j\beta i\alpha}, \quad (3.35)$$

is only valid once the onsite levels are self-consistent.

The additional pairwise repulsive function accounts for the energy contributions due to overlap repulsion, exchange-correlation, crystal field effects and nuclear-nuclear electrostatic interactions neglected in the TB Hamiltonian. For many materials a repulsive pair potential may be parametrised to reproduce important physical quantities such as the lattice parameter or elastic constants once the TB model for the electronic interactions is parameterised from the DFT bandstructure. Evaluated in accordance with the structural energy difference theorem,<sup>107</sup> it is the bond (electronic) contribution to the binding energy which distinguishes different structures.

### 3.3.4 Magnetism within TB

The LCN TB bond model has since been modified to treat both charge transfer and magnetism in a self-consistent manner.<sup>17,38,41,42</sup> Just as for the wavefunction in DFT, the LCAO basis set is extended by a further spin index,

$$\phi_{i\alpha}(\mathbf{r} - \mathbf{R}_i - \mathbf{R}) = \begin{pmatrix} \phi_{i\alpha\uparrow}(\mathbf{r} - \mathbf{R}_i - \mathbf{R}) \\ \phi_{i\alpha\downarrow}(\mathbf{r} - \mathbf{R}_i - \mathbf{R}) \end{pmatrix}, \quad (3.36)$$

where the axis of spin quantisation is defined locally at each site. Schrödinger's equation then becomes

$$\hat{H}\psi_{\nu\mathbf{k}}^{(n)}(\mathbf{r}) = E_{\mathbf{k}}^{(n)}(\mathbf{r})\psi_{\nu\mathbf{k}}^{(n)}(\mathbf{r}), \quad (3.37)$$

and the secular equation, assuming orthogonality, is written as

$$\sum_{i\alpha\mu} [H_{j\beta\nu i\alpha\mu}(\mathbf{k}) - E^{(n)}(\mathbf{k})] c_{i\alpha\mu}^{(n)}(\mathbf{k}) = 0. \quad (3.38)$$

In the simplest approximation, the effects of magnetism may be added to the Hamiltonian by modifying the onsite matrix elements only. In this case, the elements are defined as<sup>17</sup>

$$H_{i\alpha\mu i\alpha\nu} = H_{i\alpha i\alpha}^{(0)}\delta_{\mu\nu} + \mathbf{B}_{i\alpha} \cdot \boldsymbol{\sigma}_{\mu\nu} - \frac{1}{2}I_{i\alpha}\mathbf{m}_{i\alpha} \cdot \boldsymbol{\sigma}_{\mu\nu}, \quad (3.39)$$

where  $H_{i\alpha i\alpha}^{(0)}$  is the non-magnetic onsite level,  $\mathbf{B}_{i\alpha}$  is an applied local magnetic field,  $\mathbf{m}_{i\alpha}$  is the local magnetic moment,  $\boldsymbol{\sigma}$  is the vector of Pauli matrices,  $I_{i\alpha}$  is the Stoner parameter, and  $\delta_{\mu\nu}$  is the Kronecker delta. The Hamiltonian is now twice as large in each direction. Considering the four quadrants of the Hamiltonian matrix in spin-space,

$$\mathbf{H} = \begin{pmatrix} H_{11}^{(0)} + \frac{1}{2}\Delta_1^{(z)} & H_{12}^{(0)} & \cdots & \frac{1}{2}(\Delta_1^{(x)} - i\Delta_1^{(y)}) & 0 & \cdots \\ H_{21}^{(0)} & H_{22}^{(0)} + \frac{1}{2}\Delta_2^{(z)} & \cdots & 0 & \frac{1}{2}(\Delta_2^{(x)} - i\Delta_2^{(y)}) & \cdots \\ \vdots & \vdots & \ddots & \vdots & \vdots & \ddots \\ \frac{1}{2}(\Delta_1^{(x)} + i\Delta_1^{(y)}) & 0 & \cdots & H_{11}^{(0)} - \frac{1}{2}\Delta_1^{(z)} & H_{12}^{(0)} & \cdots \\ 0 & \frac{1}{2}(\Delta_2^{(x)} + i\Delta_2^{(y)}) & \cdots & H_{21}^{(0)} & H_{22}^{(0)} - \frac{1}{2}\Delta_2^{(z)} & \cdots \\ \vdots & \vdots & \ddots & \vdots & \vdots & \ddots \end{pmatrix}, \quad (3.40)$$

the diagonal elements of each quadrant are shifted by an amount dependent on the magnitude and direction of the magnetic moment and magnetic field,

$$\Delta_i^{(a)} = (B_i^{(a)} - \frac{1}{2}I_i m_i^{(a)}). \quad (3.41)$$

The intersite elements of the  $\uparrow\uparrow$  and  $\downarrow\downarrow$  quadrants are identical to those of the non-magnetic Hamiltonian, while the intersite elements of the  $\uparrow\downarrow$  and  $\downarrow\uparrow$  quadrants are zero.

Such a dependence of the onsite levels on the local magnetic moments can be derived from DFT by a second-order expansion of the exchange-correlation potential in terms of charge and magnetic moment fluctuations.<sup>17,39,106,108,109</sup> The contributions from bond charge are neglected and the Stoner integral is taken to be an atomic quantity independent of crystal structure or volume. Although the exchange interaction increases with

decreasing atomic volume, the approximation of a volume-independent Stoner integral appears to be adequate for many cases.<sup>38,110</sup>

The binding energy now acquires an extra term, the exchange energy,

$$U_X = -\frac{1}{4} \sum_i I_i m_i^2, \quad (3.42)$$

while the bond energy is calculated from the spin density matrix or spin-polarised density of states,

$$U_{Bond} = \sum_{i\alpha\mu j\beta\nu, i \neq j} \rho_{i\alpha\mu j\beta\nu} H_{j\beta\nu i\alpha\mu} = \sum_{i\alpha\nu} \int^{E_F} (E - E_{i\alpha\nu}) n_{i\alpha\nu}(E) dE. \quad (3.43)$$

This second equality only holds when the local spin direction is rotated into the direction of the magnetic moment. The binding energy just requires the addition of the magnetism-independent repulsive energy,

$$U_B = U_{Bond} + U_X + U_{Rep}. \quad (3.44)$$

The variational property of DFT is preserved in the derivation of the TB energy. Therefore, the ground state configuration may be found by shifting the onsite levels (or equivalently the charges and magnetic moments) until self-consistency is achieved. This process is identical to minimising the binding energy locally with respect to the onsite levels.<sup>17</sup> Once the self-consistent solution has been achieved, the Hellmann-Feynman theorem<sup>78,82</sup> may once again be used to determine the force on an atom. This variational property may not be exploited in traditional non-self-consistent TB models.

### 3.3.5 TB studies of iron

Various magnetically self-consistent TB band and bond models have been developed and used to study metals. Mehl & Papaconstantopoulos<sup>111</sup> confirmed that a non-magnetic

two-centre TB model, even without the constraint of orthogonality, was incapable of predicting the correct 0K structures for iron and cobalt, emphasising that it is the magnetic contribution to the energy which stabilises the ground state. Zhong *et al.*<sup>112</sup> developed a band model for iron including a Stoner description of magnetism which was able to predict the correct ground state  $\alpha$  structure and the structural energy differences to within a few percent of the *ab initio* values. The predicted elastic constants compare well with experimental and DFT calculations, as does the pressure derivative of the bulk modulus (related to the third order derivative of the total energy with respect to the lattice constant). This last quantity was highlighted as it is important in achieving the correct melting temperatures and thermal expansion coefficients. Zhong *et al.* also point out that their model would be more useful for mechanical simulations of iron than simple interatomic potentials, like the EAM, which do not contain the bonding anisotropy required to study phase stability, while still managing to be computationally efficient in comparison to *ab initio* calculations. More recently, a non-orthogonal magnetic TB model including *s*, *p*, and *d* bond integrals was used by Cohen *et al.*<sup>113</sup> to study the high pressure phases of iron employing a weakly volume-dependent Stoner integral. Interestingly, they found that AFM, rather than NM, structures in  $\gamma$  iron were stable up to pressures of about 50GPa, and that the inclusion of the AFM structures improved the fit of the Vinet equation of state with the experimental data. Such a result has also been found using more accurate DFT calculations. Cohen *et al.* also find that non-collinear structures are especially sensitive to the value of the Stoner integral, the atomic moment approximation and the levels of hybridisation between different orbital types.

In fact, Muniz *et al.*<sup>50</sup> have shown that the non-collinear behaviour of iron is highly dependent on the details of the TB bandstructure. In particular, they found that the stability of ferromagnetism over non-collinear distortions relies on the hybridisation of the *sp* and *d* bands (unlike nickel, where the behaviour is relatively insensitive to the detailed bandstructure). The behaviour is characterised by the spin-wave stiffness constant,  $D$ ,

defined by the magnon dispersion relation at long wavelengths,

$$\omega = D\mathbf{q}^2, \quad (3.45)$$

where  $\omega$  is the frequency and  $\mathbf{q}$  the wavevector of the spin-waves.  $D$  is the second derivative of the total energy of the crystal with respect to the angle of a slow, in-plane, twist of the spin lattice,

$$D = \frac{\partial^2 U_{\text{B}}}{\partial \theta^2}. \quad (3.46)$$

If  $D$  is positive at  $\mathbf{q} = 0$ , ferromagnetism is stable. For nickel,  $D$  depends on the exchange splitting of the  $d$  band alone and is both large and positive. For iron, however, Muniz *et al.* find the value of  $D$  to be unsatisfactory when calculated using  $d$  TB models, both with canonical and non-canonical TB parameters, second and third nearest neighbours, and variable values of both  $N_d$  and  $m$ . This result is consistent with Fig. 2.6 by Pettifor,<sup>32</sup> in that the ferromagnetism in nickel is strong for a nearly filled  $d$  band, but weak in the centre of the band and unstable with respect to antiferromagnetic or non-collinear distortions.

The previous models were based on the non-self-consistent formulation of the TB method, historically referred to as the ‘band model’. Liu *et al.*<sup>114</sup> published a self-consistent Stoner-like TB *bond* model for iron with enforced LCN, which was used to study point defects. The charges and magnetic moments were calculated self-consistently by iteratively shifting the onsite levels in the Hamiltonian such that the input and output magnetic moments were identical and the final charge was zero. The bulk NM DOS and structural stabilities were correctly reproduced, and the elastic constants were found to fit well with experiment. More importantly, it was found that the variation of forces and magnetic moments around a vacancy in pure iron differed between self-consistent LCN and non-self-consistent calculations. The LCN calculations were able to reproduce the oscillatory nature of the atomic relaxations in the atomic shells around a vacancy found using DFT. The fact that the results of the simulations with and without LCN

differed significantly strengthens the point that a self-consistent bond model is required for accurate atomistic simulations involving forces. However, recent work by Soin *et al.*<sup>115</sup> showed that some of Liu’s calculations could not have been converged fully with respect to  $k$ -point density, calling into question the results in the original paper.

Paxton & Finnis<sup>109</sup> developed a model for the Fe-Cr system by including magnetism in their polarizable ion TB technique, which describes the effects of charge transfer via a Hubbard U term. Two versions of the model were developed: in the first, an expansion of the Hohenberg-Kohn functional to second order about a non-magnetic reference charge density results in a Stoner-like itinerant model as outlined previously; in the second, an expansion to first order about an initial magnetic moment is used to produce a ‘fixed moment model’. The fixed moment model has proved useful in explaining anomalies in the Fe-Cr phase diagram. However, as the authors were primarily interested in details of the electronic structure, the TB model was not adjusted to reproduce the correct physical properties of the metals, such as the ground-state crystal structure of Fe.

TB models for magnetism have been extended beyond the simple Stoner implementation to include spin-orbit coupling. The works of Desjonquères, Autès, Barreteau and Spanjaard<sup>116,117</sup> have shown that spin-orbit coupling is required to study the enhancement of magnetic moments at surfaces and in one-dimensional wires, and to investigate magnetic anisotropy in low-dimensional iron structures. In particular, for very small systems like iron clusters or magnetic break-junctions, it was found that the  $d$ - $d$  intra-atomic terms had to be calculated extremely accurately within the full Hartree-Fock theory to obtain results within even the same order of magnitude as the experimental work. This implies that more accurate techniques other than TB in its current form might be required to achieve good results for low-dimensional systems.

In general, it seems that achieving accurate self-consistency in the charges and magnetic moments is a problem with current TB methods.<sup>115</sup> The naïve application of mixing methods from DFT does not always result in smooth TB convergence and so new methods must be developed.

### 3.3.6 Implementation in BOPfox and computational methodology

For the work which follows, I included the formalism described in section 3.3.4 for orthogonal magnetic TB into the Bond-Order Potentials from Oxford package, (BOPFOX).<sup>118</sup> BOPFOX is a multi-functional simulation tool capable of static energy and force calculations, structural relaxations and Molecular Dynamics using EAM, BOP and TB methods. The coding was completely general so that both collinear and non-collinear TB calculations could be performed with the spin direction on each atom constrained to lie along an initial input vector. The magnetic code was based around existing non-self-consistent non-magnetic subroutines.

Since the Tight-Binding energy is variational, a self-consistent solution to the TB secular equation, Eqn. (3.38), corresponds to a solution which minimises the total binding energy. Self-consistency is achieved by mixing the input and output charges and magnetic moments from each diagonalisation step such that a penalty,  $\zeta$ , is brought to zero. This is equivalent to solving the equation

$$\zeta(\mathbf{x}) = 0, \quad (3.47)$$

where the vector  $\mathbf{x}$  defines the inputs to the penalty,  $\mathbf{x} = (x_1, x_2, \dots, x_n)$ , and the vector  $\zeta$  contains the set of penalties

$$\zeta = (\zeta_1(x_1, x_2, \dots, x_n), \zeta_2(x_1, x_2, \dots, x_n), \dots, \zeta_n(x_1, x_2, \dots, x_n)). \quad (3.48)$$

The inputs to each new diagonalisation step are determined from the last by means of the Jacobian matrix,  $\mathbf{J}$ , where

$$\mathbf{x}_{l+1} = \mathbf{x}_l - \mathbf{J}^{-1} \zeta(\mathbf{x}_l), \quad (3.49)$$

and

$$\mathbf{J} = \begin{pmatrix} \frac{\partial \zeta_1}{\partial x_1} & \dots & \frac{\partial \zeta_1}{\partial x_n} \\ \vdots & \ddots & \vdots \\ \frac{\partial \zeta_n}{\partial x_1} & \dots & \frac{\partial \zeta_n}{\partial x_n} \end{pmatrix}. \quad (3.50)$$

Rather than calculating the Jacobian explicitly in BOPFOX, it is approximated using the Broyden iterative scheme.<sup>119</sup> A particular formulation<sup>120</sup> of Broyden's method designed to limit memory use has been implemented.

In this work we are concerned with constrained magnetic calculations with local charge neutrality, where local magnetic fields are used to fix the orientations of the spin directions at each site. In this case, the binding energy is defined by

$$\begin{aligned} U_B &= U_{\text{Bond}} + U_X + U_C + U_{\text{Rep}} \\ &= U_{\text{Bond}} - \frac{1}{4} \sum_i I_i m_i^2 + \sum_i \mathbf{B}_i^{(1)} \cdot \mathbf{m}_i + \sum_i \mathbf{B}_i^{(2)} \cdot \mathbf{m}_i + \sum_i J_i q_i^2 + U_{\text{Rep}}. \end{aligned} \quad (3.51)$$

Two local magnetic field components,  $B_i^{(1)}$  and  $B_i^{(2)}$ , are generated by projecting the output magnetic moment from each diagonalisation of the Hamiltonian onto two vectors,  $\mathbf{p}_i^{(1)}$  and  $\mathbf{p}_i^{(2)}$ , mutually perpendicular to the local input spin direction,  $\mathbf{s}_i^{(0)}$ , so that

$$B_i^{(a)} = \mathbf{m}_i \cdot \mathbf{p}_i^{(a)}. \quad (3.52)$$

The vectors  $\mathbf{p}_i^{(1)}$  and  $\mathbf{p}_i^{(2)}$  are calculated via the Gram-Schmidt process.<sup>121</sup> These local constraining fields enter the onsite levels according to Eqn. (3.39). In order to minimise this particular energy, the self-consistency penalties are defined by the difference in magnetic moments entering the Hamiltonian,  $\mathbf{m}_i^{\text{con}}$ , and those calculated from the expansion coefficients after diagonalisation,  $\mathbf{m}_i'^{\text{con}}$ ,

$$\boldsymbol{\zeta}_i^{(m)} = \mathbf{m}_i^{\text{con}} - \mathbf{m}_i'^{\text{con}}. \quad (3.53)$$

Both vectors are calculated by projecting the magnetic moment along the initial input

vector,

$$\mathbf{m}_i^{con} = \left( \mathbf{m}_i \cdot \mathbf{s}_i^{(0)} \right) \mathbf{s}_i^{(0)}. \quad (3.54)$$

Local Charge Neutrality is enforced by the further penalty function

$$\zeta_i^{(q)} = q_i = N_i - N_i^{(0)}, \quad (3.55)$$

where  $N_i$  is the number of electrons at a site and  $N_i^{(0)}$  is the reference number of electrons on the non-magnetic free atom.

Once  $\zeta = 0$ , the magnetic moments are self-consistent and the local charges at each site are zero. The constraining  $\mathbf{B}$  fields do not enter the final energy expression since they remain orthogonal to the magnetic moment direction. In this way, only the length of the magnetic moment in a given direction is allowed to vary. Completely unconstrained magnetic calculations are also possible when these additional field terms are switched off. The Coulomb energy also does not enter the self-consistent energy expression since the final  $q_i$  are zero. This means the value of the charge prefactor,  $J_i$ , entering Eqn. (3.51) is arbitrary and in practice is set to unity. The new onsite levels are, therefore, constructed at each step from the magnetic moments and charges as

$$E_{i\mu\nu} = E_i^{(0)}\delta_{\mu\nu} + \mathbf{B}_i^{(1)} \cdot \boldsymbol{\sigma}_{\mu\nu} + \mathbf{B}_i^{(2)} \cdot \boldsymbol{\sigma}_{\mu\nu} - \frac{1}{2}I_i\mathbf{m}_i \cdot \boldsymbol{\sigma}_{\mu\nu} + q_i, \quad (3.56)$$

where the orbital index,  $\alpha$ , has been dropped for simplicity. The final self-consistent LCN energy expression is given by

$$\begin{aligned} U_B &= U_{\text{Bond}} + U_X + U_{\text{Rep}} \\ &= U_{\text{Bond}} - \frac{1}{4} \sum_i I_i m_i^2 + U_{\text{Rep}}. \end{aligned} \quad (3.57)$$

The self-consistent TB procedure is explained schematically in Figure 3.2.

As for DFT, all TB calculations were performed in reciprocal space using a  $\Gamma$ -centred

$k$ -point mesh, with the number of  $k$ -points per unit cell selected to achieve convergence of the binding energy to within 1 meV/atom. The tetrahedron method with Blöchl corrections<sup>98</sup> was used to integrate across the Brillouin zone.

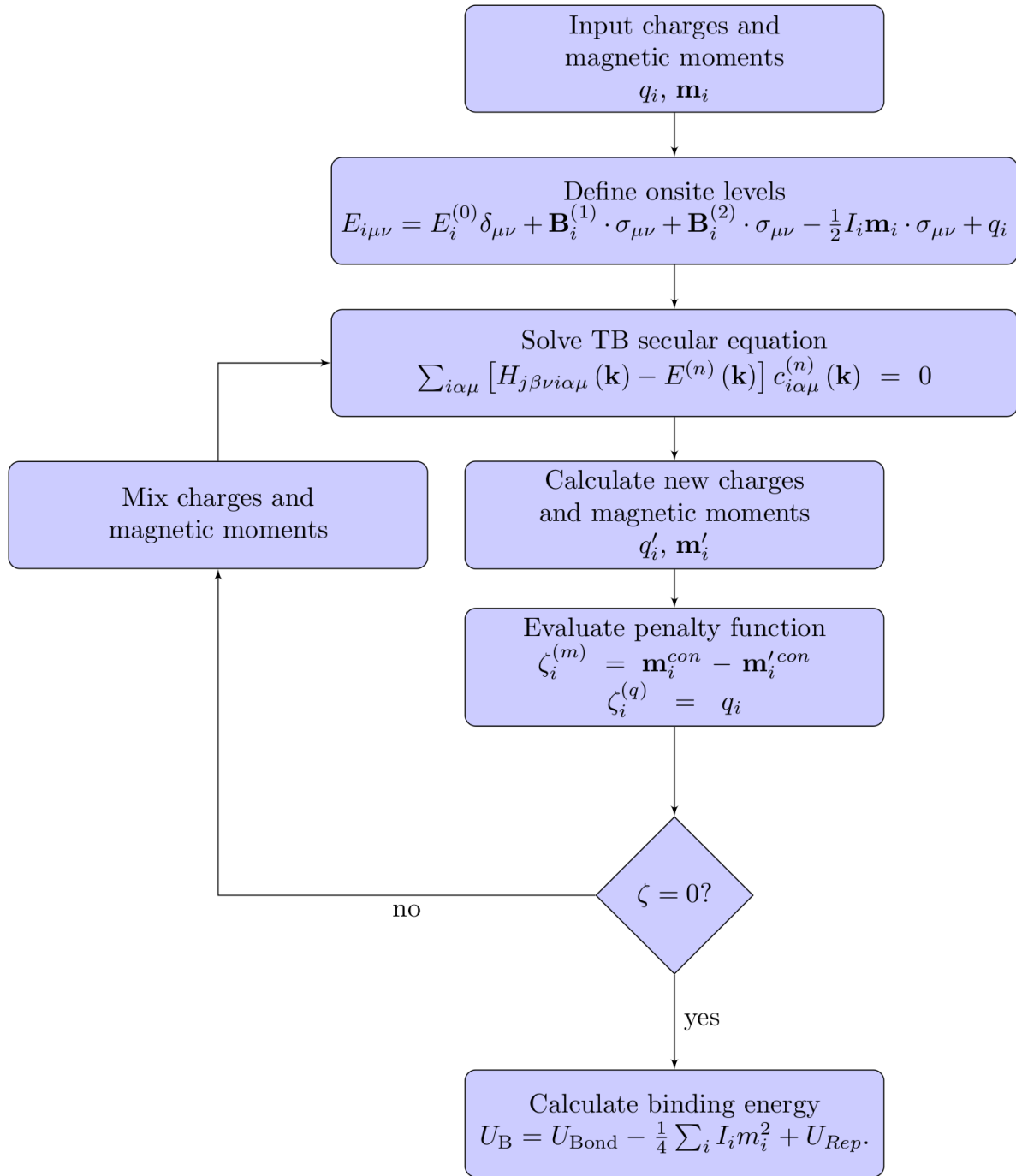


Figure 3.2: Schematic flowchart illustrating the self-consistent magnetic TB calculation.

### 3.4 Summary

Density Functional theory is an accurate quantum mechanical computational method for solving the non-relativistic time-independent manybody Schrödinger equation where the total ground state energy may be written as a unique functional of the charge density. DFT has been extended to treat collinear and non-collinear magnetism by rewriting the equations in terms of the spin density matrix, allowing charge and magnetisation densities to be calculated self-consistently. The major constraint on the accuracy of a DFT calculation is the exchange-correlation potential whose exact form remains elusive for all practical purposes. The GGA approximation to the XC functional is found to provide accurate reference data for bulk and defective iron, correctly stabilising the ferromagnetic ground state. DFT has also been used to explore more complex non-collinear magnetic structures found in  $\gamma$  and  $\epsilon$  iron. Unless otherwise stated, DFT calculations in this thesis have been performed using the VASP code.

The Tight-Binding method achieves a further simplification of the electronic structure by restricting itself to a minimal Linear Combination of Atomic Orbitals basis set and parametrising the Hamiltonian matrix elements in terms of real-space functional forms. The modern TB bond model maintains the variational property of DFT, allowing collinear and non-collinear magnetism to be treated by self-consistent modifications of the atomic onsite levels. Magnetic TB parametrisations for iron are able to account for the magnetic ground state and defect structures as observed with DFT. However, problems still remain with achieving fast and stable self-consistency, and with the inclusion of hybridisation, non-orthogonality and models for complex charge or magnetic interactions. The self-consistent magnetic TB bond method has been implemented in the BOPFOX code for this work.

# Chapter 4

## Magnetic analytic BOP: theoretical extensions

### 4.1 Introduction

The method of analytic Bond-Order Potentials (BOP) for the transition metals was derived by Drautz & Pettifor<sup>16</sup> based on the recursion method solution to TB<sup>122–124</sup> and the numerical BOP.<sup>76</sup> While all three methods involve mapping the TB Hamiltonian onto a semi-infinite one-dimensional chain, both the recursion method and numerical BOP require numerical integration techniques which are computationally slow. Drautz & Pettifor derived an analytic expression for the energy and forces by writing the local density of states as a polynomial expansion about a semi-elliptic reference function in terms of the moments of the TB DOS. At the second moment level, the behaviour of the analytic BOP is similar to an EAM or Finnis-Sinclair potential approximation; the bond energy scales in proportion to the square-root of the second moment of the density of states, although with a valence dependence missing from the simpler interatomic potentials. Higher moments include more information about the shape of the DOS or, equivalently, the bonding out to further distances in the material, with the BOP DOS converging towards to the TB result as the number of moments tends towards infinity. Recently, Drautz & Pettifor

have shown<sup>17</sup> how the analytic BOP may be extended to include the effects of charge transfer and magnetism in alignment with the self-consistent TB bond model described in chapter 3. The self-consistent calculation of charges and magnetic moments is replaced with a direct minimisation of the binding energy with respect to the Hamiltonian onsite levels. The forces have been shown to be exact derivatives of the energy at a given level of approximation, despite the approximate DOS, which is not the case for the numerical BOP. The analytic BOP method has been used to study magnetism in a simple fourth moment model where the analytic expressions could be solved relatively easily. In the work that follows, I show how the particular gradients of the energy necessary for a practical implementation can be derived. Further extensions to the analytic BOP method designed to minimise the occurrence of unphysical negative densities of states are also discussed. These include various approximations for the asymptotic recursion coefficients, as well as a hybrid method involving the damping factors of the Kernel Polynomial Method and the approximate calculation of higher-order moments.

## 4.2 Background theory

### 4.2.1 Non-magnetic analytic BOP

It is easier to understand the fundamentals of the analytic BOP method<sup>16</sup> by considering first a non-magnetic material. The important quantities we are interested in for a given crystal structure, for example the total binding energy or the local charges, may be determined from the site-projected local density of states. The  $p^{th}$  moment of the local DOS, like any distribution, is defined as

$$\mu_{i\alpha}^{(p)} = \int E^p n_{i\alpha}(E) dE. \quad (4.1)$$

Each moment contains more and more detailed information about the shape of the distribution. For example, the first moment defines the band centre, the second determines

its root mean square width, the third its skewness and the fourth its tendency towards bimodality. The complete distribution may be reconstructed from a knowledge of all of its moments. Furthermore, a Moments Theorem<sup>125</sup> relates the moments of the local DOS in particular to the topology of the local crystal structure by deriving a new expression for the moment in terms of electronic hopping paths. Assuming an orthonormal basis set, the Moments Theorem defines<sup>26</sup>

$$\mu_{i\alpha}^{(p)} = \sum_{j_1\beta_1 \dots j_{p-1}\beta_{p-1}} H_{i\alpha j_1\beta_1} H_{j_1\beta_1 j_2\beta_2} \dots H_{j_{p-1}\beta_{p-1} i\alpha}. \quad (4.2)$$

Therefore, the moment is a sum over the matrix element products contributing to individual electronic hopping paths of total length  $p$  which start and end at site  $i\alpha$ . Higher moments contain more detailed information about the topology as they involve hopping paths going out further into the crystal. While an infinite number of moments is required to reconstruct the local DOS completely, many physical trends can be explained with reference to just the first few moments.

The recursion method and the method of BOPs begin with a mapping of the real-space TB Hamiltonian onto the problem of a semi-infinite one-dimensional chain, making use of the Lanczos recursion algorithm.<sup>126</sup> The Hamiltonian then takes a tridiagonal form in the new basis. The onsite levels of the chain are  $a_n$  and nearest neighbours are connected by hopping matrix elements  $b_n$ , i.e.<sup>16</sup>

$$H_{mn} = \begin{cases} a_n & \text{if } m = n, \\ b_n & \text{if } m = n - 1, \\ b_{n+1} & \text{if } m = n + 1, \\ 0 & \text{otherwise.} \end{cases} \quad (4.3)$$

The tridiagonal matrix elements are defined by the recurrence relation (using the bra-ket state notation)<sup>16</sup>

$$\hat{H} |u_n\rangle = a_n |u_n\rangle + b_n |u_{n-1}\rangle + b_{n+1} |u_{n+1}\rangle. \quad (4.4)$$

This recursive process allows the useful mathematical properties of tridiagonal matrices to be exploited. For example, in exact TB methods, tridiagonalisation via the Lanczos algorithm is often the first step towards complete diagonalisation in a  $k$ -space calculation of the eigenvalues and eigenvectors of the Hamiltonian. The recursion method in turn takes advantage of the fact that the determinant of a tridiagonal matrix may be written exactly as a continuant, or continued fraction, to calculate the density of states in real-space from the Green's function.

The Green's function is defined in terms of the tridiagonalised Hamiltonian as<sup>83</sup>

$$G(Z)_{i\alpha j\beta} = \langle i\alpha | \left( \hat{Z} - \hat{H} \right)^{-1} | j\beta \rangle. \quad (4.5)$$

The local DOS is then constructed from the imaginary part of the diagonal elements of the Green's function,<sup>16</sup>

$$n_{i\alpha}(E) = -\frac{1}{\pi} \lim_{\eta \rightarrow \infty} \Im \{ G_{i\alpha i\alpha}(E + i\eta) \}. \quad (4.6)$$

Because of the tridiagonal nature of the Hamiltonian, the diagonal elements of the Green's function for a given starting state,  $G_{00}$ , may be written as the continued fraction<sup>16</sup>

$$G_{00}(Z) = \frac{1}{Z - a_0 - \frac{b_1^2}{Z - a_1 - \frac{b_2^2}{Z - a_2 - \frac{b_3^2}{\ddots}}}}, \quad (4.7)$$

where the  $a_n$  and  $b_n$  are the recursion coefficients of the Lanczos chain.

These recursion coefficients and the moments of the DOS are directly related. The

first few moments may be written as

$$\begin{aligned}
 \mu_{i\alpha}^{(0)} &= 1, \\
 \mu_{i\alpha}^{(1)} &= a_0, \\
 \mu_{i\alpha}^{(2)} &= a_0^2 + b_1^2, \\
 \mu_{i\alpha}^{(3)} &= a_0^3 + 2a_0b_1^2 + a_1b_1^3.
 \end{aligned} \tag{4.8}$$

Further terms may be calculated by a set of recurrence relations.<sup>127</sup> The diagonal elements of the Green's function may therefore be rewritten in terms of the electronic hopping paths.

In a practical recursion calculation the continued fraction Eqn. (4.7), which is exact, must be truncated at  $m_{max}$  levels, leading to an approximate representation for the local DOS which must be integrated numerically. This is the basis of the numerical BOP method. If, however, the recursion coefficients are assumed to take constant values throughout,  $a_\infty$  and  $b_\infty$ , then the entire continued fraction may be summed analytically such that the resultant local DOS takes the form<sup>16</sup>

$$n_{i\alpha}(E) = \frac{2}{\pi} \sqrt{1 - \left( \frac{E - a_\infty}{2b_\infty} \right)^2}. \tag{4.9}$$

This semi-elliptic form is called the second moment approximation (SMA) DOS. Choosing  $a_\infty = a_0$  and  $b_\infty = b_1$  results in the particular Finnis-Sinclair form of the EAM potential where the bond energy varies in proportion to  $\sqrt{\mu_{i\alpha}^{(2)}}$ .

The analytic BOP, however, is derived by using this exact result as the reference DOS,

$$n_{i\alpha}^{(0)}(\epsilon) = \frac{2}{\pi} \sqrt{1 - \epsilon^2}, \tag{4.10}$$

about which we take an expansion of the form

$$n_{i\alpha}(\epsilon) = n_{i\alpha}^{(0)}(\epsilon) + \delta n_{i\alpha}(\epsilon). \tag{4.11}$$

$\epsilon$  is the energy scaled according to  $\epsilon = (E - a_{i\alpha}^{(\infty)}) / (2b_{i\alpha}^{(\infty)})$  such that the DOS forms a band between  $\epsilon = \pm 1$ .

The Chebyshev polynomials of the second kind<sup>128</sup> are chosen as the basis for the expansion of  $\delta n_{i\alpha}(\epsilon)$  since these are the polynomial eigenstates of the semi-infinite chain with constant recursion coefficients and so are orthonormal to this particular choice of  $n_{i\alpha}^{(0)}$ . Expanding the DOS with respect to the Chebyshev polynomials of the first kind and choosing a different weight function leads to the related Kernel Polynomial Method.<sup>129</sup> The polynomials of the second kind are chosen since the square-root DOS is a reasonable approximation for close-packed metallic systems. The Finnis-Sinclair model may be viewed as the lowest order approximation to the BOPs and the BOPs may be seen as a systematic extension of the Finnis-Sinclair model. The DOS is then given, up to a number of moments  $n_{\max}$ , by<sup>16</sup>

$$n_{i\alpha}(\epsilon) = \frac{2}{\pi} \sqrt{1 - \epsilon^2} \left[ \sum_{m=0}^{n_{\max}} \sigma_{i\alpha}^{(m)} P_m(\epsilon) \right]. \quad (4.12)$$

The Chebyshev polynomials are defined by

$$P_m(\epsilon) = \sum_{n=0}^m p_{mn} \epsilon^n, \quad (4.13)$$

where

$$p_{(m+1)n} = 2p_{m(n-1)} - p_{(m-1)n} \quad (4.14)$$

unless  $n < 0$  or  $n > m$  when  $p_{mn} = 0$ . The expansion coefficients,  $\sigma_{i\alpha}^{(m)}$ , are found according to<sup>16</sup>

$$\sigma_{i\alpha}^{(m)} = \sum_{n=0}^m p_{mn} \hat{\mu}_{i\alpha}^{(n)}, \quad (4.15)$$

using the orthogonality conditions of the Chebyshev polynomials,

$$\int P_m(\epsilon) P_n(\epsilon) \sqrt{1 - \epsilon^2} d\epsilon = \delta_{mn}, \quad (4.16)$$

where  $\delta_{mn}$  is the Kronecker delta. The  $\hat{\mu}_{i\alpha}^{(n)}$  are the dimensionless moments,

$$\hat{\mu}_{i\alpha}^{(n)} = \int_{-1}^1 \epsilon^n n_{i\alpha}(\epsilon) d\epsilon, \quad (4.17)$$

which can be calculated as

$$\hat{\mu}_{i\alpha}^{(n)} = \frac{1}{(2b_{i\alpha}^{(\infty)})} \sum_{l=0}^n \binom{n}{l} (-1)^l (a_{i\alpha}^{(\infty)})^l \mu_{i\alpha}^{(n-l)}. \quad (4.18)$$

The semi-elliptic reference DOS is a valid starting point for a calculation when the true TB DOS forms one connected band; this is no longer appropriate for materials with band gaps, or molecules where the exact DOS may consist of delta functions, since in practice the Chebyshev polynomial expansion will lead to negative values of the DOS.

In many ways the expansion coefficients  $\sigma_{i\alpha}^{(m)}$  are the most critical parameters which enter the BOP expressions and they depend explicitly on the local topology through the moments of the DOS. The expansion coefficients may therefore be written directly in terms of the recursion coefficients. Within the so-called linear approximation, where higher-order terms of  $\gamma_{i\alpha m}$  and  $\delta_{i\alpha m}$  are neglected, the expansion coefficients are given by

$$\sigma_{i\alpha}^{(0)} = 1, \quad (4.19)$$

$$\sigma_{i\alpha}^{(2m)} = \delta_{i\alpha m} = (b_{i\alpha m}^2 - b_{i\alpha}^{(\infty)2}) / b_{i\alpha}^{(\infty)2}, \quad (4.20)$$

$$\sigma_{i\alpha}^{(2m+1)} = \gamma_{i\alpha m} = (a_{i\alpha m} - a_{i\alpha}^{(\infty)}) / a_{i\alpha}^{(\infty)}, \quad (4.21)$$

for  $m \geq 1$ . More complex, exact expressions for the expansions may be derived, but the linear approximation has been shown to capture enough of the local topology to differentiate the 6-moment densities of states of the common bulk metallic crystal structures.<sup>16</sup> Several methods have been developed to approximate the asymptotic recursion coefficients,  $a_{i\alpha}^{(\infty)}$  and  $b_{i\alpha}^{(\infty)}$ , which will be discussed in more detail in section 4.3.3.

The benefit of taking this polynomial expansion is that now the expression for the local

DOS, Eqn. (4.12), may be integrated *analytically*. Defining the set of response functions,  $\hat{\chi}$ , as

$$\hat{\chi}_1(\phi_F) = 1 - \frac{\phi_F}{\pi} + \frac{1}{2\pi} \sin(2\phi_F) \quad (4.22)$$

$$\hat{\chi}_n(\phi_F) = \frac{1}{\pi} \left[ \frac{\sin(n+1)\phi_F}{n+1} - \frac{\sin(n-1)\phi_F}{n-1} \right] \text{ for } n \geq 2, \quad (4.23)$$

where the Fermi phase  $\phi_{F,i\alpha} = \cos^{-1} \left[ (E_F - a_{i\alpha}^{(\infty)}) / (2b_{i\alpha}^{(\infty)}) \right]$ , the number of electrons may then be written as

$$N_{i\alpha} = 2 \int^{E_F} n_{i\alpha}(E) dE = 2 \sum_{m=0}^{n_{max}} \sigma_{i\alpha}^{(m)} \hat{\chi}_{m+1}(\phi_{F,i\alpha}), \quad (4.24)$$

and the bond energy as

$$U_{i\alpha}^{Bond} = 2 \int^{E_F} (E - E_{i\alpha}) n_{i\alpha}(E) dE \quad (4.25)$$

$$= 2b_{i\alpha}^{(\infty)} \sum_{m=0}^{n_{max}} \sigma_{i\alpha}^{(m)} [\hat{\chi}_{m+2}(\phi_{F,i\alpha}) - \gamma_{0i\alpha} \hat{\chi}_{m+1}(\phi_{F,i\alpha}) + \hat{\chi}_m(\phi_{F,i\alpha})], \quad (4.26)$$

where  $\gamma_{0i\alpha} = (E_{i\alpha} - a_{i\alpha}^{(\infty)}) / b_{i\alpha}^{(\infty)}$  and  $\hat{\chi}_0 = 0$ . These quantities may be determined directly from the moments without first calculating and integrating the DOS. The  $\hat{\chi}$  introduce the explicit valence-dependence of the bond energy missing from SMA EAM or F-S models.

## 4.2.2 Collinear magnetism within analytic BOP

### Energy and magnetic moments

The case of a collinearly magnetic material (ferromagnetic, antiferromagnetic or ferrimagnetic) is particularly simple because a global axis for spin quantisation may be defined. If the magnetic moment on each atom is taken to lie along a global  $z$  direction then, in the absence of spin-orbit coupling, the  $\uparrow\uparrow$  and  $\downarrow\downarrow$  spin channels decouple and we define two spin bands,  $\uparrow$  and  $\downarrow$ , which may be expanded separately in terms of their moments within

the analytic BOP theory. In essence, each equation from section 4.2.1 acquires one new spin index as shown by Drautz & Pettifor.<sup>17</sup>

The moments of the local spin DOS are given by

$$\mu_{i\alpha\nu}^{(p)} = \int E^p n_{i\alpha\nu}(E) dE = \sum_{\substack{i_1\alpha_1, \\ i_2\alpha_2, \\ \dots, \\ i_{p-1}\alpha_{p-1}}} H_{i\alpha\nu i_1\alpha_1\nu} H_{i_1\alpha_1\nu i_2\alpha_2\nu} \dots H_{i_{p-1}\alpha_{p-1}\nu i\alpha\nu}. \quad (4.27)$$

Taking a BOP expansion about the reference DOS for each spin channel, the number of electrons may be written down as

$$N_{i\alpha\nu} = \int^{E_F} n_{i\alpha\nu}(E) dE = \sum_{m=0}^{n_{max}} \sigma_{i\alpha\nu}^{(m)} \hat{\chi}_{m+1}(\phi_{F,i\alpha\nu}), \quad (4.28)$$

while the bond energy is given by

$$U_{i\alpha\nu}^{Bond} = \int^{E_F} (E - E_{i\alpha\nu}) n_{i\alpha\nu}(E) dE \quad (4.29)$$

$$= b_{i\alpha\nu}^{(\infty)} \sum_{m=0}^{n_{max}} \sigma_{i\alpha\nu}^{(m)} [\hat{\chi}_{m+2}(\phi_{F,i\alpha\nu}) - \gamma_{0,i\alpha\nu} \hat{\chi}_{m+1}(\phi_{F,i\alpha\nu}) + \hat{\chi}_m(\phi_{F,i\alpha\nu})]. \quad (4.30)$$

The integrated response functions are still defined according to Eqn. (4.23) while  $\gamma_{0,i\alpha\nu}$  is

$$\gamma_{0,i\alpha\nu} = \left( E_{i\alpha\nu} - a_{i\alpha\nu}^{(\infty)} \right) / b_{i\alpha\nu}^{(\infty)}, \quad (4.31)$$

and the local Fermi phase is

$$\phi_{F,i\alpha\nu} = \cos^{-1} \left[ \left( E_F - a_{i\alpha\nu}^{(\infty)} \right) / \left( 2b_{i\alpha\nu}^{(\infty)} \right) \right]. \quad (4.32)$$

The expansion coefficients for each band are given by

$$\sigma_{i\alpha\nu}^{(\infty)} = \sum_{n=0}^m p_{mn} \hat{\mu}_{i\alpha\nu}^{(n)}, \quad (4.33)$$

with the reduced moments defined by

$$\hat{\mu}_{i\alpha\nu}^{(n)} = \frac{1}{(2b_{i\alpha\nu}^{(\infty)})^n} \sum_{l=0}^n \binom{n}{l} (-1)^l (a_{i\alpha\nu}^{(\infty)})^l \mu_{i\alpha\nu}^{(n-l)}. \quad (4.34)$$

The local magnetic moment may be calculated from the difference in the numbers of up- and down-spin electrons on an atomic site according to

$$m_i = \sum_{\alpha} (N_{i\alpha\uparrow} - N_{i\alpha\downarrow}) = \sum_{\alpha} \sum_{m=0}^{n_{max}} \sigma_{i\alpha\uparrow}^{(m)} \hat{\chi}_{m+1}(\phi_{F,i\alpha\uparrow}) - \sum_{\alpha} \sum_{m=0}^{n_{max}} \sigma_{i\alpha\downarrow}^{(m)} \hat{\chi}_{m+1}(\phi_{F,i\alpha\downarrow}). \quad (4.35)$$

Since the two spin bands may be treated separately, the calculation of the band filling and bond energy for a particular set of input charges and magnetic moments (or, equivalently, onsite levels) will take only twice as long as a non-magnetic calculation.

### Gradients and forces

While the variational properties of DFT and TB ensure that a self-consistent set of charges and magnetic moments defines a stationary point in the total energy, this relationship breaks down for low-moment BOP expansions where the DOS is evaluated approximately. In order that the BOP energies and forces remain consistent for physically sensible MD simulations, the true stationary point of the binding energy must be found by a direct minimisation with respect to the charges and magnetic moments or, equivalently, the onsite levels,<sup>17</sup>

$$\sum_{i\alpha\nu} \frac{\partial U_B}{\partial E_{i\alpha\nu}} = 0. \quad (4.36)$$

The binding energy in Eqn. (3.44) may be differentiated with respect to a general parameter  $\Lambda$  as

$$\frac{dU_B}{d\Lambda} = \frac{dU_{\text{Bond}}}{d\Lambda} + \frac{dU_X}{d\Lambda} + \frac{dU_{\text{Rep}}}{d\Lambda}. \quad (4.37)$$

Drautz & Pettifor<sup>17</sup> have shown how these analytic derivatives are obtained from the local DOS valid for both BOP and TB, although they have not derived explicit expressions in

terms of the BOP parameters. The bond energy is defined as

$$U_{\text{Bond}} = \sum_{i\alpha\nu} \int^{E_F} (E - E_{i\alpha\nu}) n_{i\alpha\nu}(E) dE, \quad (4.38)$$

and so the derivative with respect to  $\Lambda$  is found as

$$\begin{aligned} \frac{dU_{\text{Bond}}}{d\Lambda} &= \sum_{i\alpha\nu} (E_F - E_{i\alpha\nu}) n_{i\alpha\nu}(E_F) \\ &\quad - \sum_{i\alpha\nu} \frac{dE_{i\alpha\nu}}{d\Lambda} \int^{E_F} n_{i\alpha\nu}(E) dE \\ &\quad + \sum_{i\alpha\nu} \int^{E_F} (E - E_{i\alpha\nu}) \frac{dn_{i\alpha\nu}(E)}{d\Lambda} dE. \end{aligned} \quad (4.39)$$

The derivative of the Fermi level may be determined by considering conservation of charge,

$$\sum_{i\alpha\nu} \frac{dN_{i\alpha\nu}}{d\Lambda} = \sum_{i\alpha\nu} n_{i\alpha\nu}(E_F) \frac{dE_F}{d\Lambda} + \sum_{i\alpha\nu} \int^{E_F} \frac{dn_{i\alpha\nu}(E)}{d\Lambda} dE = 0. \quad (4.40)$$

Thus the derivative of the bond energy is obtained as

$$\begin{aligned} \frac{dU_{\text{Bond}}}{d\Lambda} &= \sum_{i\alpha\nu} \int^{E_F} (E - E_F) \frac{dn_{i\alpha\nu}(E)}{d\Lambda} dE \\ &\quad - \sum_{i\alpha\nu} \left( E_{i\alpha\nu} - \frac{\sum_{j\beta\mu} E_{j\beta\mu} n_{j\beta\mu}(E_F)}{\sum_{j\beta\mu} n_{j\beta\mu}(E_F)} \right) \int^{E_F} \frac{dn_{i\alpha\nu}(E)}{d\Lambda} dE \\ &\quad - \sum_{i\alpha\nu} N_{i\alpha\nu} \frac{dE_{i\alpha\nu}}{d\Lambda}. \end{aligned} \quad (4.41)$$

Similarly, the derivative of the exchange energy is

$$\frac{dU_X}{d\Lambda} = -\frac{1}{2} \sum_{i\alpha\nu} \left( (-1)^\nu I_i m_{i\alpha} - \frac{\sum_{j\beta\mu} (-1)^\mu I_j m_{j\beta} n_{j\beta\mu}(E_F)}{\sum_{j\beta\mu} n_{j\beta\mu}(E_F)} \right) \int^{E_F} \frac{dn_{i\alpha\nu}(E)}{d\Lambda} dE. \quad (4.42)$$

The Stoner integral is assumed to have no  $\Lambda$ -dependence. Importantly, these derivatives

can be rewritten in terms of the moments according to Eqn. (134) in Ref. [17] so that

$$\frac{dU_B}{d\Lambda} = \sum_{i\alpha\nu} \sum_{n=0}^{n_{\max}} w_{i\alpha\nu}^{(n)} \frac{d\mu_{i\alpha\nu}^{(n)}}{d\Lambda} - \sum_{i\alpha\nu} N_{i\alpha\nu} \frac{dE_{i\alpha\nu}}{d\Lambda} + \frac{dU_{\text{rep}}}{d\Lambda}. \quad (4.43)$$

The prefactors  $w_{i\alpha\nu}^{(n)}$ , which we call the *weights*, are the derivatives of the binding energy with respect to the moments,

$$w_{i\alpha\nu}^{(n)} = \frac{\partial U_B}{\partial \mu_{i\alpha\nu}^{(n)}}. \quad (4.44)$$

The weights take the form

$$w_{i\alpha\nu}^{(n)} = \frac{\partial U_{\text{band}}}{\partial \mu_{i\alpha\nu}^{(n)}} + \left( E_{i\alpha\nu} - \frac{\sum_{j\beta\mu} E_{j\beta\mu} n_{j\beta\mu}(E_F)}{\sum_{j\beta\mu} n_{j\beta\mu}(E_F)} \right. \\ \left. - \frac{1}{2} \left( (-1)^\nu I_i m_i - \frac{\sum_{j\beta\mu} (-1)^\mu I_j m_j n_{j\beta\mu}(E_F)}{\sum_{j\beta\mu} n_{j\beta\mu}(E_F)} \right) \right) \frac{\partial}{\partial \mu_{i\alpha\nu}^{(n)}} \int^{E_F} n_{i\alpha\nu} dE, \quad (4.45)$$

if the band and onsite contributions to the bond energy are separated.

The expression for the total derivative of the energy is condensed into a Hellmann-Feynman-like form by defining a ‘bond-order’ term  $\tilde{\Theta}_{i\alpha\nu j\beta\nu}$ ,<sup>17</sup>

$$\tilde{\Theta}_{i\alpha\nu j\beta\nu} = \sum_{n=1}^{n_{\max}} \Xi_{i\alpha\nu j\beta\nu}^{(n-1,n)}, \quad (4.46)$$

where  $\Xi_{i\alpha\nu j\beta\nu}^{(n-1,n)}$  is calculated from the weights and Hamiltonian as

$$\Xi_{i_1\alpha_1\nu i_n\alpha_n\nu}^{(n-1,m)} = \sum_{i_2 i_3 \dots i_{n-1}} \sum_{\alpha_2 \alpha_3 \dots \alpha_{n-1}} \left( \sum_{l=1}^n w_{i_l\alpha_l\nu}^{(m)} \right) H_{i_1\alpha_1\nu i_2\alpha_2\nu} H_{i_2\alpha_2\nu i_3\alpha_3\nu} \\ \dots H_{i_{n-1}\alpha_{n-1}\nu i_n\alpha_n\nu}, \quad (4.47)$$

such that

$$\frac{dU_{\text{Bond}}}{d\Lambda} = \sum_{i\alpha j\beta} \sum_{\nu} \tilde{\Theta}_{i\alpha\nu j\beta\nu} \frac{dH_{j\beta\nu i\alpha\nu}}{d\Lambda}. \quad (4.48)$$

Replacing  $\Lambda$  with  $E_{i\alpha\nu}$ , we reach an expression for the gradients of the energy with respect

to the onsite levels,

$$\frac{dU_B}{dE_{i\alpha\nu}} = \tilde{\Theta}_{i\alpha\nu i\alpha\nu} - N_{i\alpha\nu}. \quad (4.49)$$

Alternatively, replacing  $\frac{d}{d\Lambda}$  with the gradient due to displacing an atom  $k$  in real space,  $\nabla_k$ , leads to an expression for the force,

$$F_k = -\nabla_k U_B = - \sum_{i\beta\nu}^{i\alpha \neq j\beta} \tilde{\Theta}_{i\alpha\nu j\beta\nu} \nabla_k H_{j\beta\nu i\alpha\nu} + \nabla_k U_{\text{rep}}, \quad (4.50)$$

valid only once the gradients defined by Eqn. (4.49) are zero.

As further shown by Drautz & Pettifor, the  $\Xi_{i\alpha\nu j\beta\nu}^{(n-1,n)}$  may be calculated iteratively. We introduce the transfer matrix,  $T_{i\alpha\nu j\beta\nu}^{(n-1,m)}$ , defined by

$$\Xi_{i\alpha\nu j\beta\nu}^{(n-1,m)} = T_{i\alpha\nu j\beta\nu}^{(n-1,m)} + w_{i\alpha\nu}^{(m)} \xi_{i\alpha\nu j\beta\nu}^{(n-1)}, \quad (4.51)$$

where  $\xi_{i\alpha\nu j\beta\nu}^{(n)}$  is the interference path

$$\xi_{i\alpha\nu j\beta\nu}^{(n)} = \langle i\alpha\nu | \hat{H}^n | j\beta\nu \rangle = \sum_{\substack{k_1\gamma_1, \\ k_2\gamma_2, \\ \dots, \\ k_{n-1}\gamma_{n-1}}} H_{i\alpha\nu k_1\gamma_1\nu} H_{i_1\alpha_1\nu k_2\gamma_2\nu} \dots H_{i_{n-1}\alpha_{n-1}\nu j\beta\nu}. \quad (4.52)$$

Subsequent values of the transfer matrices may be determined from previous levels by

$$T_{i\alpha\nu j\beta\nu}^{(n,m)} = \sum_{k\gamma} H_{i\alpha\nu k\gamma\nu} \left( T_{k\gamma\nu j\beta\nu}^{(n-1,m)} + w_{k\gamma\nu}^{(m)} \xi_{k\gamma\nu j\beta\nu}^{(n-1)} \right). \quad (4.53)$$

Note the additional bracket missing from Eqn. (146) in Ref. [17], required for a correct calculation of the transfer matrices.

### 4.2.3 Previous BOP studies

Drautz & Pettifor<sup>16</sup> used a simple canonical  $d$  TB parametrisation (where the  $dd\sigma : dd\pi : dd\delta$  bond integrals are given in the ratio  $-6 : 4 : -1$ ) where the asymptotic recursion co-

efficients were defined globally, with  $a^{(\infty)} = a_1$  and  $b^{(\infty)} = b_1$ , to test the properties of the non-magnetic analytic BOP method. For this case they evaluated the bond energy contribution to the binding energy of the common bcc, fcc and hcp structures as a function of band-filling across the transition metals and found this to be consistent with the Moments Theorem prediction of Ducastelle<sup>30</sup> and Cyrot-Lackmann.<sup>125</sup> The reference DOS of the Lanczos chain is identical for these three structures and the bond energy is found to vary parabolically with band-filling, reproducing the general behaviour observed in the 4d and 5d series. The fourth moment is the first contribution to differentiate between bcc and the close-packed structures, while 6 moments are required to separate hcp and fcc. Therefore, by 6 moments the BOP expansion is able to reproduce the hcp→bcc→hcp→fcc structural trend across the series.

The non-magnetic BOP DOS was also used to evaluate the stable ferromagnetic moment in each structure in accordance with the second Stoner criterion, Eqn. (2.14). The general behaviour of the magnetic moments as a function of volume compares well to the exact TB results, although fine details of the DOS structure, particularly close to the Fermi level, would be required for numerical accuracy. Until now the magnetic analytic BOP method had not been tested in comparison with a complete TB model for any material.

Recently the *numerical* BOP method has also been extended to model collinear magnetic systems by including a spin-dependence along the same lines as analytic BOP. Mrovec *et al.*<sup>77</sup> have shown that the numerical BOP provides an accurate description of the electronic and magnetic structure of iron at 0K when combined with a suitable parametrisation. In order to achieve numerical accuracy with DFT and experiment, the TB parameters have been refitted for a 9-moment numerical BOP model. However, it is known that the approximate calculation of the DOS in the numerical BOP method leads to an inaccuracy in the Hellmann-Feynman forces such that the energy and forces are inconsistent for low moment expansions.<sup>17</sup> Furthermore, these calculations still require the slow numerical integration which prompted the development of the analytic method.

### 4.3 Extensions to the theory

#### 4.3.1 BOP derivatives

For an efficient computational implementation of the analytic magnetic BOP, the derivatives defined in section 4.2.2 for the general case must be derived analytically for the BOP density of states. By substituting in the explicit BOP expansion for the band energy, we find that

$$\begin{aligned}
\frac{\partial U_{\text{Band}}}{\partial \mu_{i\alpha\nu}^{(n)}} &= \frac{\partial}{\partial \mu_{i\alpha\nu}^{(n)}} \sum_{m=0}^{n_{\text{max}}} \left( b_{i\alpha\nu}^{(\infty)} \sigma_{i\alpha\nu}^{(m)} [\hat{\chi}_{m+2} - 2\epsilon_{\text{F},i\alpha\nu} \hat{\chi}_{m+1} + \hat{\chi}_m] \right) \\
&= \sum_{m=0}^{n_{\text{max}}} \left( \frac{\partial b_{i\alpha\nu}^{(\infty)}}{\partial \mu_{i\alpha\nu}^{(n)}} \sigma_{i\alpha\nu}^{(m)} [\hat{\chi}_{m+2} - 2\epsilon_{\text{F},i\alpha\nu} \hat{\chi}_{m+1} + \hat{\chi}_m] \right. \\
&\quad \left. + b_{i\alpha\nu}^{(\infty)} \left( \frac{\partial \sigma_{i\alpha\nu}^{(m)}}{\partial \mu_{i\alpha\nu}^{(n)}} + \frac{\partial \sigma_{i\alpha\nu}^{(m)}}{\partial a_{i\alpha\nu}^{(\infty)}} \frac{\partial a_{i\alpha\nu}^{(\infty)}}{\partial \mu_{i\alpha\nu}^{(n)}} + \frac{\partial \sigma_{i\alpha\nu}^{(m)}}{\partial b_{i\alpha\nu}^{(\infty)}} \frac{\partial b_{i\alpha\nu}^{(\infty)}}{\partial \mu_{i\alpha\nu}^{(n)}} \right) [\hat{\chi}_{m+2} - 2\epsilon_{\text{F},i\alpha\nu} \hat{\chi}_{m+1} + \hat{\chi}_m] \right) \\
&\quad + b_{i\alpha\nu}^{(\infty)} \sigma_{i\alpha\nu}^{(m)} \left[ \frac{\partial \hat{\chi}_{m+2}}{\partial a_{i\alpha\nu}^{(\infty)}} - 2 \frac{\partial \epsilon_{\text{F},i\alpha\nu}}{\partial a_{i\alpha\nu}^{(\infty)}} \hat{\chi}_{m+1} - 2\epsilon_{\text{F},i\alpha\nu} \frac{\partial \hat{\chi}_{m+1}}{\partial a_{i\alpha\nu}^{(\infty)}} + \frac{\partial \hat{\chi}_m}{\partial a_{i\alpha\nu}^{(\infty)}} \right] \frac{\partial a_{i\alpha\nu}^{(\infty)}}{\partial \mu_{i\alpha\nu}^{(n)}} \\
&\quad + b_{i\alpha\nu}^{(\infty)} \sigma_{i\alpha\nu}^{(m)} \left[ \frac{\partial \hat{\chi}_{m+2}}{\partial b_{i\alpha\nu}^{(\infty)}} - 2 \frac{\partial \epsilon_{\text{F},i\alpha\nu}}{\partial b_{i\alpha\nu}^{(\infty)}} \hat{\chi}_{m+1} - 2\epsilon_{\text{F},i\alpha\nu} \frac{\partial \hat{\chi}_{m+1}}{\partial b_{i\alpha\nu}^{(\infty)}} + \frac{\partial \hat{\chi}_m}{\partial b_{i\alpha\nu}^{(\infty)}} \right] \frac{\partial b_{i\alpha\nu}^{(\infty)}}{\partial \mu_{i\alpha\nu}^{(n)}} \Bigg). \tag{4.54}
\end{aligned}$$

Equivalently, taking the BOP expansion for the number of electrons,  $N_{i\alpha\nu}$ , we find that

$$\begin{aligned}
\frac{\partial}{\partial \mu_{i\alpha\nu}^{(n)}} \int^{E_{\text{F}}} n_{i\alpha\nu} dE &= \frac{\partial}{\partial \mu_{i\alpha\nu}^{(n)}} N_{i\alpha\nu} \\
&= \frac{\partial}{\partial \mu_{i\alpha\nu}^{(n)}} \sum_{m=0}^{n_{\text{max}}} \sigma_{i\alpha\nu}^{(m)} \hat{\chi}_{m+1} (\phi_{\text{F},i\alpha\nu}) \\
&= \sum_{m=0}^{n_{\text{max}}} \left( \left( \frac{\partial \sigma_{i\alpha\nu}^{(m)}}{\partial \mu_{i\alpha\nu}^{(n)}} + \frac{\partial \sigma_{i\alpha\nu}^{(m)}}{\partial a_{i\alpha\nu}^{(\infty)}} \frac{\partial a_{i\alpha\nu}^{(\infty)}}{\partial \mu_{i\alpha\nu}^{(n)}} + \frac{\partial \sigma_{i\alpha\nu}^{(m)}}{\partial b_{i\alpha\nu}^{(\infty)}} \frac{\partial b_{i\alpha\nu}^{(\infty)}}{\partial \mu_{i\alpha\nu}^{(n)}} \right) \hat{\chi}_{m+1} (\phi_{\text{F},i\alpha\nu}) \right. \\
&\quad \left. + \sigma_{i\alpha\nu}^{(m)} \left( \frac{\partial \hat{\chi}_{m+1}}{\partial a_{i\alpha\nu}^{(\infty)}} \frac{\partial a_{i\alpha\nu}^{(\infty)}}{\partial \mu_{i\alpha\nu}^{(n)}} + \frac{\partial \hat{\chi}_{m+1}}{\partial b_{i\alpha\nu}^{(\infty)}} \frac{\partial b_{i\alpha\nu}^{(\infty)}}{\partial \mu_{i\alpha\nu}^{(n)}} \right) \right). \tag{4.55}
\end{aligned}$$

The calculation of derivatives of the energy is thus broken down into the partial derivatives of the various BOP parameters  $a_{i\alpha\nu}^{(\infty)}$ ,  $b_{i\alpha\nu}^{(\infty)}$ ,  $\sigma_{i\alpha\nu}^{(m)}$ ,  $\hat{\chi}_m$ , and the Fermi level  $\epsilon_{\text{F},i\alpha\nu}$ , whose

precise forms are known for any given analytic approximation to  $a_{i\alpha\nu}^{(\infty)}$  and  $b_{i\alpha\nu}^{(\infty)}$ .

The expansion coefficients are differentiated by writing them in terms of the reduced moments,  $\hat{\mu}_{i\alpha\nu}^{(k)}$ :

$$\frac{\partial \sigma_{i\alpha\nu}^{(m)}}{\partial \mu_{i\alpha\nu}^{(n)}} = \sum_{k=n}^m p_{mk} \frac{\partial \hat{\mu}_{i\alpha\nu}^{(k)}}{\partial \mu_{i\alpha\nu}^{(n)}} = \sum_{k=n}^m \frac{p_{mk}}{(2b_{i\alpha\nu}^{(\infty)})^k} \binom{k}{n} \left(-a_{i\alpha\nu}^{(\infty)}\right)^{(k-n)}, \quad (4.56)$$

$$\frac{\partial \sigma_{i\alpha\nu}^{(m)}}{\partial a_{i\alpha\nu}^{(\infty)}} = \sum_{k=0}^m p_{mk} \frac{\partial \hat{\mu}_{i\alpha\nu}^{(k)}}{\partial a_{i\alpha\nu}^{(\infty)}} = - \sum_{k=n}^m \frac{p_{mk}}{(2b_{i\alpha\nu}^{(\infty)})^k} \sum_{n=0}^{k-1} (k-n) \binom{k}{n} \mu_{i\alpha\nu}^{(n)} \left(-a_{i\alpha\nu}^{(\infty)}\right)^{(k-n-1)}, \quad (4.57)$$

and

$$\frac{\partial \sigma_{i\alpha\nu}^{(m)}}{\partial b_{i\alpha\nu}^{(\infty)}} = \sum_{k=0}^m p_{mk} \frac{\partial \hat{\mu}_{i\alpha\nu}^{(k)}}{\partial b_{i\alpha\nu}^{(\infty)}} = - \sum_{k=1}^m n \frac{p_{mk}}{b_{i\alpha\nu}^{(\infty)}} \hat{\mu}_{i\alpha\nu}^{(n)}. \quad (4.58)$$

The derivatives of the response functions may be rewritten in terms of the Fermi phase by the chain rule,

$$\frac{\partial \hat{\chi}_m}{\partial a_{i\alpha\nu}^{(\infty)}} = \frac{\partial \hat{\chi}_m}{\partial \cos(\phi_{F,i\alpha\nu})} \frac{\partial \cos(\phi_{F,i\alpha\nu})}{\partial a_{i\alpha\nu}^{(\infty)}}, \quad (4.59)$$

$$\frac{\partial \hat{\chi}_m}{\partial b_{i\alpha\nu}^{(\infty)}} = \frac{\partial \hat{\chi}_m}{\partial \cos(\phi_{F,i\alpha\nu})} \frac{\partial \cos(\phi_{F,i\alpha\nu})}{\partial b_{i\alpha\nu}^{(\infty)}}, \quad (4.60)$$

where the definitions of the response functions then lead to

$$\frac{\partial \hat{\chi}_m}{\partial \cos(\phi_{F,i\alpha\nu})} = - \frac{1}{\pi \sin(\phi_{F,i\alpha\nu})} [\cos(m+1)\phi_{F,i\alpha\nu} - \cos(m-1)\phi_{F,i\alpha\nu}], \quad (4.61)$$

$$\frac{\partial \cos(\phi_{F,i\alpha\nu})}{\partial a_{i\alpha\nu}^{(\infty)}} = - \frac{1}{2b_{i\alpha\nu}^{(\infty)}}, \quad (4.62)$$

$$\frac{\partial \cos(\phi_{F,i\alpha\nu})}{\partial b_{i\alpha\nu}^{(\infty)}} = - \frac{\cos(\phi_{F,i\alpha\nu})}{2b_{i\alpha\nu}^{(\infty)}}. \quad (4.63)$$

The derivatives of the recursion coefficients will depend on the particular approximation as discussed in section 4.3.3. These derivatives may be used to calculate the gradients of the energy with respect to the onsite levels according to Eqn. (4.49), and the forces according to Eqn. (4.50). The forces are numerically exact derivatives of the energy once

the energy has been minimised with respect to the onsite levels.

### 4.3.2 Local charge neutrality

Since the BOP self-consistent solution does not coincide with a stationary point in the energy, the LCN condition may not be maintained in the same manner as for TB methods. Instead, a further onsite-only Coulomb term is added to the energy, equivalent to a Hubbard  $U$  term, which modifies the onsite levels according to

$$H_{i\alpha\nu i\alpha\nu} = H_{i\alpha\nu i\alpha\nu}^X + J_i q_i. \quad (4.64)$$

$H_{i\alpha\nu i\alpha\nu}^X$  are the onsite levels containing the exchange and magnetic field terms defined by Eqn. (3.39) only, and  $q_i$  is the total charge on an atom defined as the difference between the number of electrons at site  $i$ ,  $N_i$ , and the reference number of electrons of the uncharged atom, in this case  $N_d$ ,

$$q_i = N_i - N_d. \quad (4.65)$$

The expression for the binding energy now acquires an additional Coulomb term

$$U_B = U_{Bond} + U_X + U_C + U_{Rep}, \quad (4.66)$$

where

$$U_C = \frac{1}{2} \sum_i J_i q_i^2. \quad (4.67)$$

This Coulomb repulsion discourages excess charge from building up on an atom and the value of  $J_i$  may be increased until a condition of LCN is enforced to a given level of numerical accuracy. This extra term introduces another derivative,

$$\frac{dU_C}{d\Lambda} = \sum_{i\alpha} \left( J_i q_i - \frac{\sum_{j\beta} J_j q_j n_{j\beta}(E_F)}{\sum_{j\beta} n_{j\beta}(E_F)} \right) \int^{E_F} \frac{dn_{i\alpha}(E_F)}{d\Lambda} dE \quad (4.68)$$

which is added to the weights given by Eqn. (4.45) for the calculation of the gradients and forces.

The effect of including  $J_i$  in a BOP calculation is shown in Fig. 4.1. Increasing  $J_i$  from zero, the local charge transfer is quickly suppressed. The Coulomb component of the energy varies as  $q_i^2$  and so the binding energy converges very rapidly with increasing  $J_i$  for most cases. However, for structures with highly distorted local densities of states, such as are found in non-collinear magnetic calculations, larger values of  $J_i$  may be required to enforce local charge neutrality.

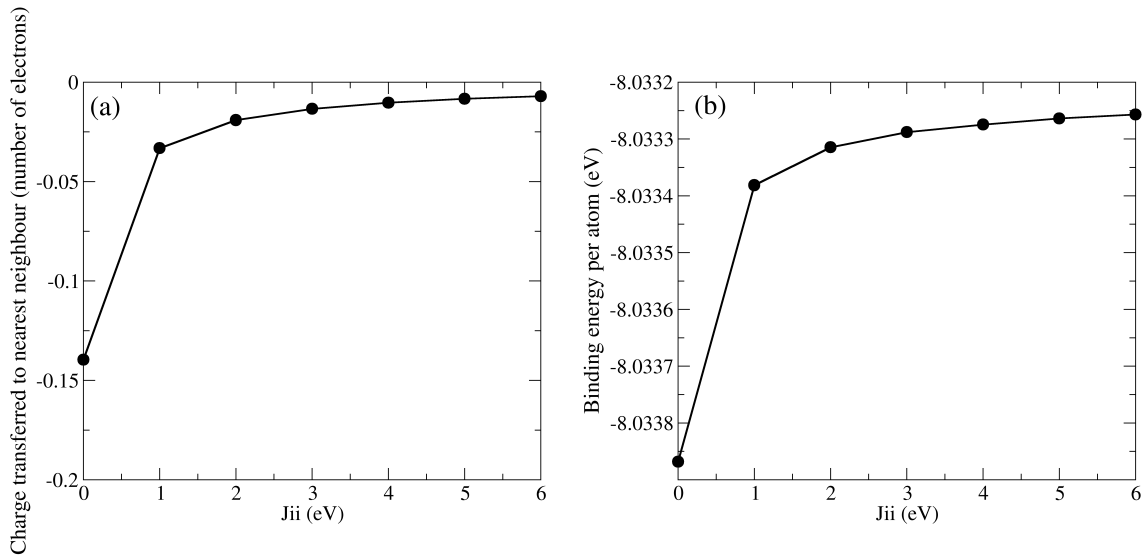


Figure 4.1: Calculation for a vacancy inside a 53-atom FM bcc Fe supercell. (a) shows the number of electrons transferred to the first nearest neighbour of the vacancy as a function of  $J_i$  as calculated with 9-moment BOP. (b) shows the variation of the total binding energy per atom in the cell as a function of  $J_i$ .

### 4.3.3 Asymptotic recursion coefficients

As mentioned in section 4.2.1, the parameters  $a^{(\infty)}$  and  $b^{(\infty)}$  (and so the expansion coefficients  $\sigma_{i\alpha\nu}^{(m)}$ ) are in many ways key to determining the shape of the expanded DOS. Unfortunately, there is no known method to derive general analytic expressions for these asymptotic values. The coefficients may be defined precisely for the TB DOS calculated by a direct diagonalisation of the Hamiltonian –  $a_{TB}$  is the centre of the band and  $b_{TB}$  is

one quarter of the bandwidth – so that, dropping the site indices for simplicity, the energies at the top and bottom of the band are given by

$$E_{Top} = a_{TB} + 2b_{TB} \quad (4.69)$$

and

$$E_{Bottom} = a_{TB} - 2b_{TB}. \quad (4.70)$$

The raw recursion coefficients of the Lanczos chain,  $a_n$  and  $b_n$ , converge towards these exact values. Thus the use of  $a^{(\infty)} = a_{TB}$  and  $b^{(\infty)} = b_{TB}$  would be justified if the continued fraction of the recursion method were evaluated to an infinite number of levels. Since in practice the fraction is terminated after just a few recursion levels (or a low number of moments), these exact values may not, in fact, be ideal. Indeed, it has been shown that although the recursion coefficients converge rapidly for simple densities of states such as the skew rectangular band, they are not well-converged even after 20 recursions (40 moments) for more realistic structures such as the canonical  $d$  band in fcc.<sup>130</sup> The task is therefore to define the  $a^{(\infty)}$  and  $b^{(\infty)}$  which provide the best representation of the DOS *for a given level*.

It has been shown<sup>130</sup> within the recursion method that if the bandwidth,  $W$ , defined by the choice of  $a^{(\infty)}$  and  $b^{(\infty)}$ , is too small this will lead to spurious delta functions outside the main band, reducing the weight in the real band; that is to say, the calculated band will not hold the correct number of electrons. Conversely, a  $W$  which is too large preserves the total weight in the band but leads to strong oscillations throughout such that the energy may not be a correct function of the band-filling. As the bandwidth tends to infinity, the DOS tends to a series of delta functions within the limits defined by the top and bottom of the exact TB band.

Beer<sup>130</sup> devised a method for determining the critical values of  $a^{(\infty)}$  and  $b^{(\infty)}$  such that the weight and shape of the DOS is reproduced as best as possible for a given level of recursion. Beer's method relies on diagonalising a matrix of recursion coefficients whose

size grows with the number of levels,

$$\mathbf{M} = \begin{pmatrix} \frac{1}{2}(a_0 - a) & \frac{1}{2}b_1 & 0 & \cdots \\ \frac{1}{2}b_1 & \frac{1}{2}(a_1 - a) & \frac{1}{2}b_2 & \cdots \\ 0 & \frac{1}{2}b_2 & \frac{1}{2}(a_2 - a) & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix}. \quad (4.71)$$

The parameter  $a$  is varied until the lowest and highest eigenvalues,  $\beta$ , are equal, at which point  $a^{(\infty)} = a$  and  $b^{(\infty)} = \beta$ . In a practical dynamic simulation, this process would have to be performed for every atom at every time step. Since there is no general *analytic* solution to this problem for a given  $n$  recursion levels which could be used to determine the derivatives with respect to the moments, these must be determined numerically. Even with  $n = 2$  the determinant of  $\mathbf{M}$  is given by a cubic function of both  $a_n$  and  $b_n$ . Beer's method is, therefore, not suitable for an analytic BOP.

The DOS in the standard analytic BOP method is not constrained to be positive. While not physical, this is a natural consequence of using a polynomial expansion. In the original analytic BOP paper,<sup>16</sup> Drautz & Pettifor show that the negative regions of the DOS are small and restricted to the band edges for the major transition metal structures. It was therefore assumed that they would not interfere with any treatment of elements or alloys with Fermi levels falling in the central regions of the band (Groups III-VIII). As will be shown in chapter 7, however, regions of negative DOS are possible in the centre of the band in non-collinear magnetic configurations. This is also true for certain defect structures dependent on the TB parametrisation (as will be shown in section 6.2). Furthermore, even when the negative regions are restricted to the band edges, they may be significant enough to alter sensitive energy differences between structures, such as the defect formation energies.

The effect of varying the bandwidth on the analytic BOP DOS is demonstrated in Fig. 4.2. A TB DOS for non-magnetic bcc iron, (a), is compared to the corresponding

9-moment analytic BOP DOS calculated using: (b) the exact TB values  $a_{TB}$  and  $b_{TB}$ , (c)  $a_{TB}$  and  $0.95b_{TB}$ , and (d)  $a_{TB}$  and  $1.2b_{TB}$ . While it appears that the exact TB values give a reasonable representation of this DOS, there are regions of negative density for all three BOP calculations. Strong oscillations are particularly evident in the DOS when the value of  $b^{(\infty)}$  is too low. Large values of  $b^{(\infty)}$  lead to smaller oscillations out to larger bandwidths and a loss of structure in the centre of the band.

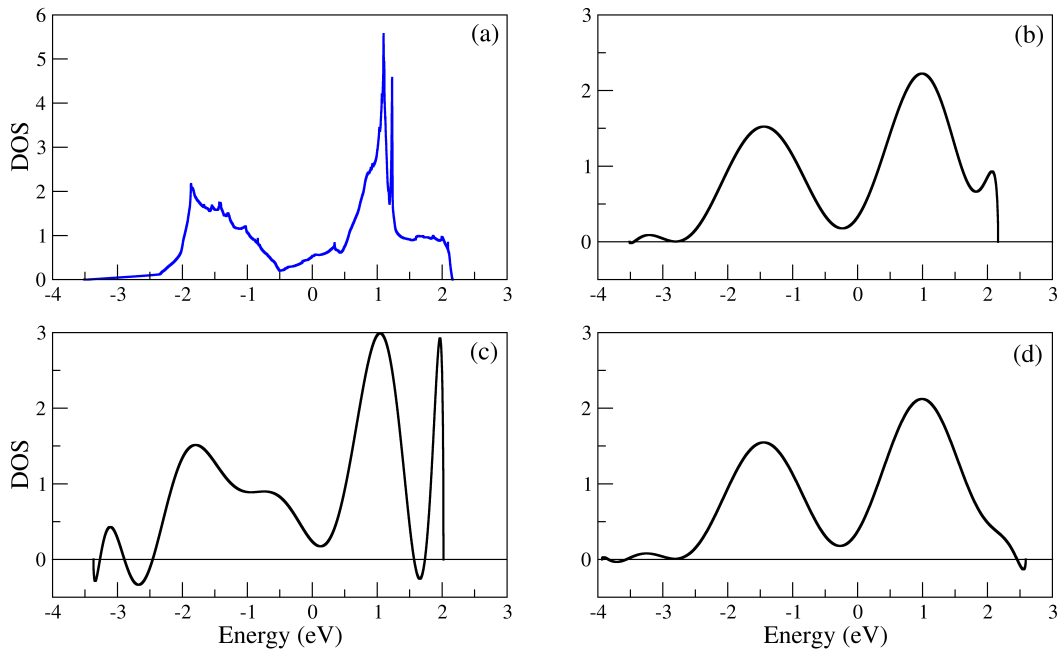


Figure 4.2: DOS for non-magnetic bcc Fe as calculated with (a) TB, (b) BOP with exact asymptotic recursion coefficients  $a^{(\infty)} = a_{TB}$  and  $b^{(\infty)} = b_{TB}$ , (c)  $a^{(\infty)} = a_{TB}$  and  $b^{(\infty)} = 0.95b_{TB}$ , and (d)  $a^{(\infty)} = a_{TB}$  and  $b^{(\infty)} = 1.2b_{TB}$ .

Several different methods for approximating  $a^{(\infty)}$  and  $b^{(\infty)}$  have been tested. The method of Haydock & Johannes<sup>131</sup> is an average of the  $(n - 1)^{\text{th}}$  and  $(n - 2)^{\text{th}}$  values of  $a$  and  $b$  for a given  $n$  levels of recursion. A new method has also been derived taking the linearized expansion coefficients, Eqn. (4.21), as a starting point. The polynomial expansion which has the smallest perturbation from the reference DOS should be achieved

when  $\sum_m (\sigma^{(m)})^2$  is minimised with respect to  $a^{(\infty)}$  and  $b^{(\infty)}$ ,

$$\frac{d}{da^{(\infty)}} \sum_m (\sigma^{(m)})^2 = \frac{d}{db^{(\infty)}} \sum_m (\sigma^{(m)})^2 = 0. \quad (4.72)$$

Substituting the linear expressions for  $\sigma^{(m)}$ , Eqn.(4.21), this leads to the following simple approximations for  $a^{(\infty)}$  and  $b^{(\infty)}$ ,

$$a^{(\infty)} = \frac{1}{m_{\text{rec}} + 1} \sum_{m=0}^{m_{\text{rec}}} a_m, \quad (4.73)$$

and

$$b^{(\infty)2} = \frac{1}{m_{\text{rec}}} \sum_{m=1}^{m_{\text{rec}}} b_m^2. \quad (4.74)$$

The recursion level,  $m_{\text{rec}}$ , is determined from the maximum number of moments used in the expansion,  $n_{\text{max}}$ , by  $m_{\text{rec}} = n_{\text{max}}/2$  if  $n_{\text{max}}$  is even, otherwise  $m_{\text{rec}} = (n_{\text{max}} - 1)/2$ .

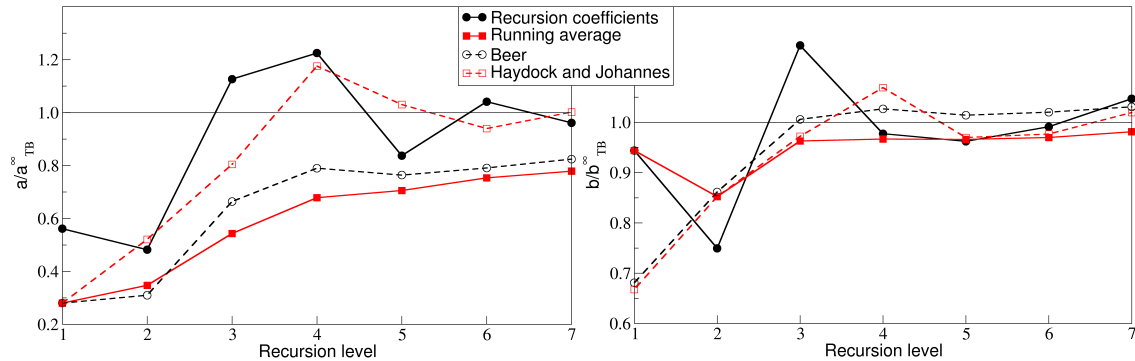


Figure 4.3: Recursion coefficients (solid circle) and approximations for  $a^{(\infty)}$  and  $b^{(\infty)}$  by running average (solid square), Beer's method<sup>130</sup> (dashed circle) and Haydock & Johannes's method<sup>131</sup> (dashed square) as function of recursion level. Calculation is for a non-magnetic bcc Fe structure with all values normalised with respect to exact TB result. Ninth moment BOP calculation ( $n_{\text{max}} = 9$ ) uses up to fourth recursion level ( $m_{\text{rec}} = 4$ ).

The results of the simple averaging method are compared to the methods of Beer and of Haydock & Johannes in Fig. 4.3. All three methods show the general behaviour of converging towards the true  $a_{TB}$  and  $b_{TB}$ . Although Haydock and Johannes's method converges most rapidly, it is also unstable to any sudden changes in the raw  $a_n$  and  $b_n$ . As

already stated, rapid convergence towards the true TB values is not necessarily the best characteristic of a method and will not always lead to the best BOP expansion at a given level, particularly for low moments. The running average method is designed to minimise divergence from the reference DOS, which is one of many possible definitions for a best expansion. This method also avoids the instabilities associated with short averages of the Haydock and Johannes type and is both analytic and computationally efficient, unlike Beer's method.

As shown in section 5.3, the simple averaging method produces good results for the bulk magnetic structures of iron. However, the problem of negative DOS is encountered for defect calculations as well as for the non-collinear magnetic BOP of chapter 7. This problem spurred the development of an adaptation to the analytic BOP borrowed from the Kernel Polynomial Method.<sup>129</sup>

#### 4.3.4 Strictly positive DOS

The negative DOS associated with the polynomial method of the analytic BOPs may be removed by integrating features of the related Kernel Polynomial Method<sup>129</sup> (KPM). Like the analytic BOP, the KPM reconstructs the local DOS from its moments by an expansion in terms of the Chebyshev polynomials of the *first* kind. Fundamentally the two methods are equivalent since the Chebyshev polynomials of the *second* kind,  $P_n(\epsilon)$ , as used in the analytic BOP, are related to those of the first kind,  $T_n(\epsilon)$ , by<sup>128</sup>

$$(1 - \epsilon^2) P_n(\epsilon) = \frac{1}{2} (T_{n+2}(\epsilon) - T_n(\epsilon)). \quad (4.75)$$

The Chebyshev polynomials may be written in trigonometric functional form and so an expansion in terms of a Chebyshev basis is formally equivalent to a Fourier series under a change of variable.<sup>132</sup> One consequence is that techniques developed for Fourier series are also applicable to Chebyshev expansions; a second consequence is that Chebyshev methods will suffer from the same practical problems as Fourier series, particularly the

phenomenon of Gibbs ringing near the location of discontinuities in the function being approximated.

Within the KPM the approximate local DOS is written as the product of a kernel,  $K^{n_{\max}}(\epsilon, \epsilon')$ , and the true DOS,

$$n_{i\alpha}^{n_{\max}}(\epsilon) = \int K^{n_{\max}}(\epsilon, \epsilon') n_{i\alpha}(\epsilon') d\epsilon'. \quad (4.76)$$

The kernel is chosen such that the approximate DOS is smooth, that is to say that the Gibbs oscillations at the band edges are damped.  $K^{n_{\max}}(\epsilon, \epsilon')$  is also chosen to be positive, ensuring the positivity of  $n_{i\alpha}^{n_{\max}}(\epsilon)$  since  $n_{i\alpha}(\epsilon')$  must also always be positive. Following the KPM, Seiser *et al.*<sup>18</sup> have expanded the kernel in terms of the Chebyshev polynomials of the second kind,

$$K^{n_{\max}}(\epsilon, \epsilon') = \frac{2}{\pi} \sqrt{1 - \epsilon^2} \left( g_P^{(0)} + \sum_{n=1}^{n_{\max}} g_P^{(n)} P_n(\epsilon) P_n(\epsilon') \right), \quad (4.77)$$

rewriting the approximate DOS as

$$n_{i\alpha}^{(n_{\max})}(\epsilon) = \frac{1}{\pi} \frac{1}{\sqrt{1 - \epsilon^2}} \left( g_P^{(0)} + \sum_{n=1}^{n_{\max}} g_P^{(n)} \sigma_{i\alpha}^{(n)} P_n(\epsilon) \right). \quad (4.78)$$

$g_P^{(n)}$  is defined as

$$g_P^{(n)} = \frac{g_T^{(n+1)}}{g_T^{(1)}}, \quad (4.79)$$

where  $g_T^{(n)}$  is known as the Jackson kernel,<sup>129</sup>

$$g_T^{(n)} = \frac{n_{\max} - n + 1}{n_{\max} + 1} \left( \cos \pi \frac{n}{n_{\max} + 1} + \sin \pi \frac{n}{n_{\max} + 1} \cot \pi \frac{1}{n_{\max} + 1} \right). \quad (4.80)$$

The kernels are designed to minimise the appearance of fluctuations or Gibbs ringing at points where the true DOS is not infinitely differentiable. Various kernels have been derived which ensure positivity of the final DOS and convergence to the true DOS with an

infinite number of levels. The Jackson kernel, in particular, also minimises the difference between the approximate DOS and the true DOS at each level of expansion and leads to the smallest broadening of sharp features, without destroying the convergence properties of the polynomial expansion.<sup>133</sup>

The smoothing effects of the Jackson kernel are dramatic. Fig. 4.4 compares the 9-moment non-magnetic bcc DOS calculated with the kernel switched on and off. The effective damping of the expansion coefficients leads to a loss of detailed shape, and hence structural information, from the DOS. It is clear that the kernel BOP method will converge more slowly towards the exact TB result and so more moments are required for a given level of structural differentiation. Although the exact calculation of higher moments must be avoided if the method is to be applied to any kind of practical dynamic simulations, they may in fact be approximated since they are damped significantly by the kernel. The only constraint is that the approximate higher moments are consistent with the exact lower moments and that they characterise a strictly positive DOS.

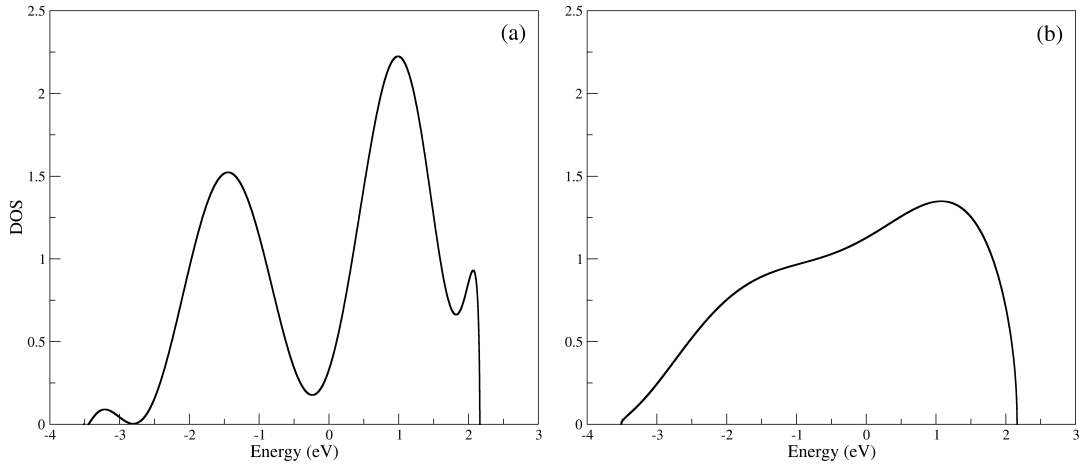


Figure 4.4: 9-moment BOP DOS for non-magnetic bcc iron calculated (a) without a kernel and (b) with the Jackson kernel. The exact  $a_{TB}^{(\infty)}$  and  $b_{TB}^{(\infty)}$  are used. The Jackson kernel smears out much of the structure from the 9-moment DOS.

These fictitious moments are calculated by once again mapping the Hamiltonian on to a semi-infinite chain. The recursion coefficients (and hence moments) are calculated

exactly up to  $m_{\text{rec}}^{\text{max}}(n_{\text{max}})$ . Beyond this level the  $a_n$  and  $b_n$  are assumed to take constant values, an approximation used in both the recursion method and numerical BOP. We define an interference path along the chain as<sup>18</sup>

$$\zeta_k^{(n)} = \langle u_k | P_n(\hat{h}) | u_0 \rangle, \quad (4.81)$$

where  $\hat{h}$  is the Hamiltonian operator along the Lanczos chain. Since the Chebyshev polynomials of the second kind may be constructed according to the recurrence relation

$$P_{n+1}(\epsilon) = 2\epsilon P_n(\epsilon) - P_{n-1}(\epsilon), \quad (4.82)$$

the interference path is written as

$$\zeta_k^{(n+1)} = 2 \left( \hat{a}_k \zeta_k^{(n)} + \hat{b}_k \zeta_{k-1}^{(n)} + \hat{b}_{k+1} \zeta_{k+1}^{(n)} \right) - \zeta_k^{(n-1)}, \quad (4.83)$$

where  $\hat{a}_k = (a_k - a^{(\infty)})/(2b^{(\infty)})$  and  $\hat{b}_k = b_k/(2b^{(\infty)})$ . The expansion coefficients may then be defined directly in terms of the interference paths as

$$\sigma_{i\alpha}^{(n)} = \langle i\alpha | P_n(\hat{h}) | i\alpha \rangle. \quad (4.84)$$

The recursion coefficients are calculated precisely up to  $m_{\text{rec}}^{\text{max}}$ , after which they are approximated as constant values. These are generally taken to be  $a^{(\infty)}$  and  $b^{(\infty)}$ , according to whichever approximation is chosen. Since the DOS is now positive, the analytic BOP result converges towards the numerical BOP DOS, which also has constant  $a_n$  and  $b_n$  beyond  $m_{\text{rec}}^{\text{max}}$ , as more and more fictitious moments are added, so long as the definition of  $b^{(\infty)}$  is large enough. As more exact moments are included, the expansion converges towards the true TB DOS. The averaged definitions for  $a^{(\infty)}$  and  $b^{(\infty)}$  defined by Equations (4.73) and (4.74) often lead to too small a bandwidth for this method.

One simple method to ensure that the bandwidth is always large enough is found by

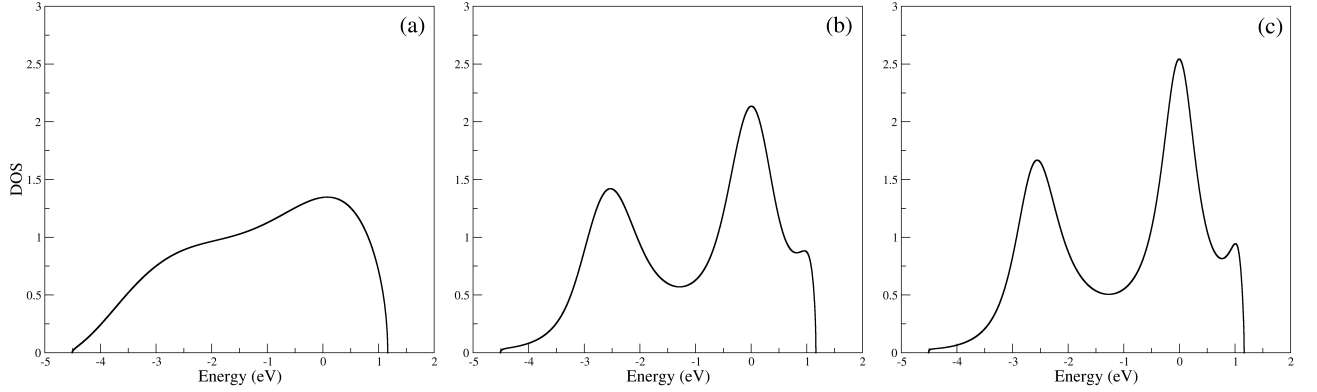


Figure 4.5: 9-moment BOP DOS calculated with  $a_{TB}^{(\infty)}$  and  $b_{TB}^{(\infty)}$  and the Jackson kernel with (a) no fictitious moments, (b) 20 fictitious moments, and (c) 50 fictitious moments. The additional moments, calculated from the Lanczos chain with constant recursion coefficients, add structure back to the damped 9-moment DOS whilst ensuring that the distribution remains positive everywhere. The Fermi level is taken as the zero of the energy scale with 6.8 electrons per atom.

calculating the maximum possible bandwidth from the known recursion coefficients. We define  $E_{\text{Top}}^{\text{max}}$  and  $E_{\text{Bottom}}^{\text{min}}$  such that

$$E_{\text{Top}}^{\text{max}} = \max(a_n + 2b_n), \quad (4.85)$$

$$E_{\text{Bottom}}^{\text{min}} = \min(a_n - 2b_n), \quad (4.86)$$

and define  $a^{(\infty)}$  and  $b^{(\infty)}$  as

$$a^{(\infty)} = \frac{1}{2} (E_{\text{Top}}^{\text{max}} + E_{\text{Bottom}}^{\text{min}}), \quad (4.87)$$

$$b^{(\infty)} = \frac{1}{4} (E_{\text{Top}}^{\text{max}} - E_{\text{Bottom}}^{\text{min}}). \quad (4.88)$$

Since, however, for many DOS the initial  $a_n$  and  $b_n$  show large deviations from the converged  $a_{TB}$  and  $b_{TB}$ , this method may lead to problems due to overestimating the bandwidth for low-moment expansions. An alternative method is found in the application of Gershgorin's circle theorem.<sup>134</sup> The theorem proves that the eigenvalues,  $\lambda$ , of a matrix,

$\mathbf{A}$ ,

$$\mathbf{A} = \begin{pmatrix} a_{11} & a_{12} & \cdots \\ a_{21} & a_{22} & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix}, \quad (4.89)$$

must lie in the regions defined by

$$|\lambda - a_{ii}| \leq \sum_{j \neq i} |a_{ij}|. \quad (4.90)$$

The eigenvalues of the linear-chain Hamiltonian, therefore, must lie within  $a_0 \pm b_1$ ,  $a_1 \pm (b_1 + b_2)$ ,  $a_2 \pm (b_2 + b_3)$ , and so on.  $a^{(\infty)}$  and  $b^{(\infty)}$  may then be chosen by the minimum  $E_{\text{Bottom}}$  and the maximum  $E_{\text{Top}}$  defined by the union of these eigenvalue bands along the energy axis. The resultant bandwidth will be equal to or smaller than that defined by the simple maximum possible bandwidth described previously.

In Fig. 4.5 it can clearly be seen that the additional moments reintroduce the DOS structure which was lost on application of the Jackson kernel, while preserving positivity. Importantly, the added computational time required to generate these fictitious moments is negligible because of the recurrence relation Eqn. (4.83). The number of additional moments required in a calculation must be determined such that the energy is appropriately converged. In practice, 250 additional moments or more are required to converge the energy to within 1 meV (see Fig. 4.6) for bcc Fe, possibly due to the strong peak in the particular DOS.

In the following chapter we will see that the analytic BOP method is able to reproduce the bulk properties of a TB model accurately without the Jackson kernel. The kernel, however, becomes necessary for defect and non-collinear calculations. Calculations using this damped BOP method will be referred to as BOP+.

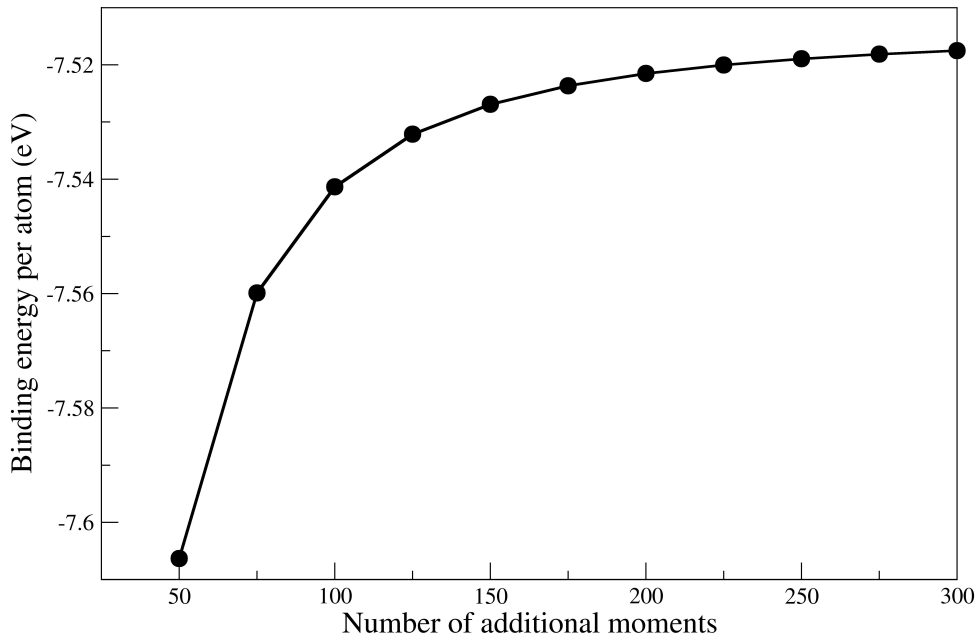


Figure 4.6: The binding energy per atom for non-magnetic bcc iron as a function of the number of additional moments used along with the Jackson kernel in the BOP calculation. 250 additional moments are required for the energy to be converged within 1 meV.

## 4.4 Implementation in BOPfox

The analytic BOP method was implemented in the BOPFOX package making use of existing non-magnetic subroutines to calculate the moments and perform the BOP expansion. The major additions to the code concern the calculation of the weights, gradients and forces, as well as the loops required to minimise the energy using an appropriate mixing method. The calculation of the site-dependent recursion coefficients from the moments was added since previous BOP calculations have relied on global definitions for  $a^{(\infty)}$  and  $b^{(\infty)}$ .

For the majority of calculations, the same Broyden mixing procedure as described in section 3.3.6 was used to update the onsite levels at each step such that the energy is minimised. For the magnetic BOP, the penalty functions which must be brought to zero

are now the gradients of the energy with respect to the onsite levels, rather than the difference in magnetic moments and charges between self-consistency steps,

$$\zeta_{i\nu}^{(\text{BOP})} = \frac{dU_{\text{B}}}{dE_{i\nu}}. \quad (4.91)$$

The mixing scheme generates a new set of onsite levels at each step, taking into account the size of these gradients such that a stationary point in the energy is achieved when  $\zeta_{i\nu}^{(\text{BOP})} = 0$ . The BOP energy minimisation procedure is explained schematically in Figure 4.7.

In general, a tolerance of  $10^{-4}$  in the self-consistent charges and magnetic moments is sufficient to converge the TB energy to within  $10^{-7}$  eV (see Figure 4.8). This is consistent with recommendations for the spin-density self-consistency tolerance in DFT calculations.<sup>135</sup> The numerical gradients of the TB energy with respect to the onsite levels are found to be below  $10^{-3}$  for this tolerance. Figure 4.9 shows the convergence of the BOP binding energy for an AFM bcc cell as a function of the gradient tolerance. Below a tolerance of  $10^{-3}$ , equivalent to the TB condition of self-consistency to  $10^{-4}$ , the BOP energy is converged to within  $10^{-5}$  eV.

As previously stated, the BOP energy is not variational, and the self-consistent and energy-minimising solutions will not be the same for low-moment expansions. In Figure 4.10 (a), the magnetic moment at the local energy minimum for an AFM bcc cell is plotted as a function of the number of moments in the BOP expansion and compared to the exact TB value. As the number of moments is increased, the BOP magnetic moment approaches the self-consistent TB value. In part (b), the difference between the magnetic moment equivalent to the onsite level exchange splitting at the energetic minimum given by Eqn. (2.1),

$$m_i = \frac{1}{I} \left( E_i^{\uparrow} - E_i^{\downarrow} \right), \quad (4.92)$$

and the resultant magnetic moment from the BOP expansion,  $m'_i$ , are plotted as a function of the number of moments. If the BOP energy were variational then  $|m_i - m'_i| = 0$  at the

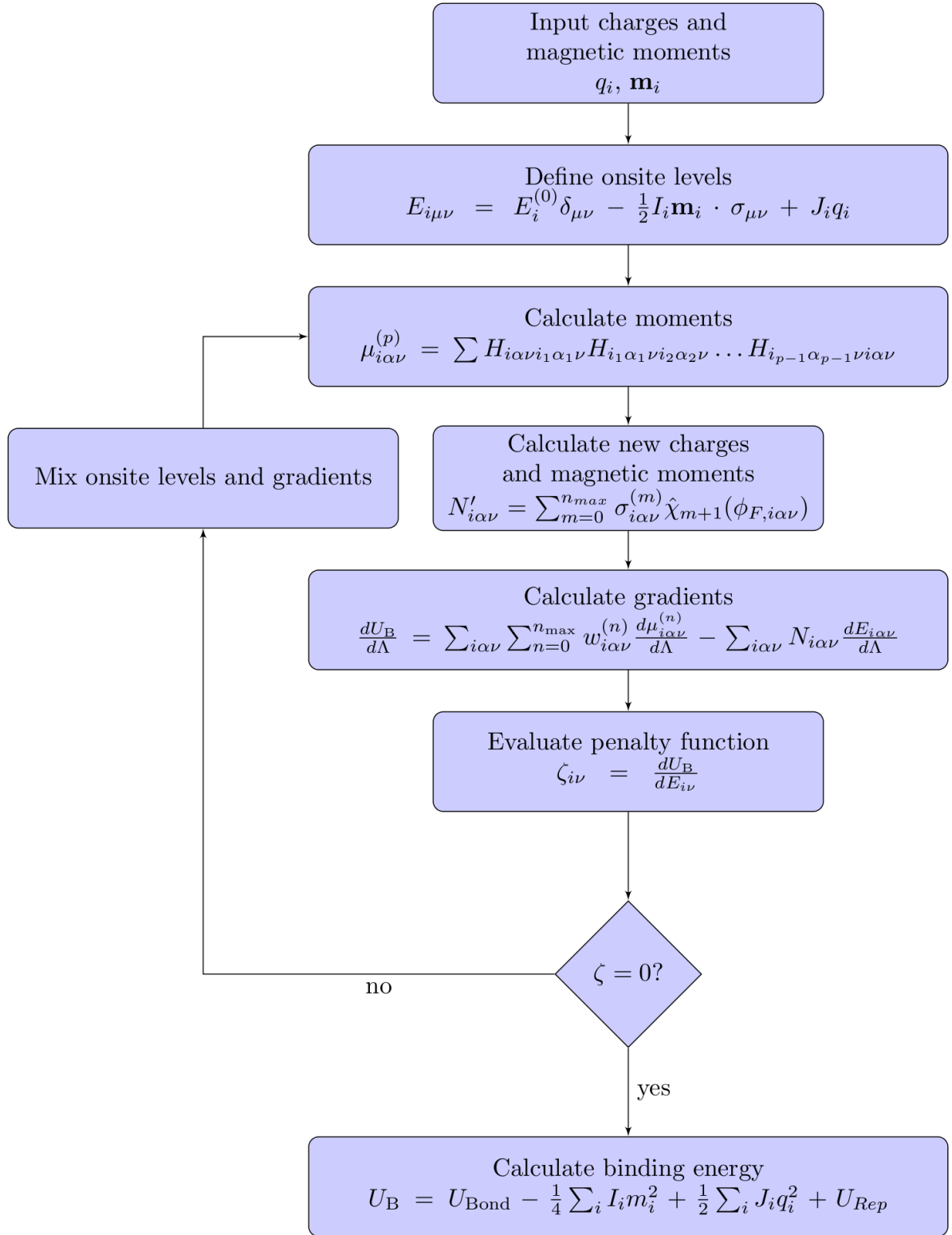


Figure 4.7: Schematic flowchart illustrating the energy minimisation procedure for a magnetic analytic BOP calculation.

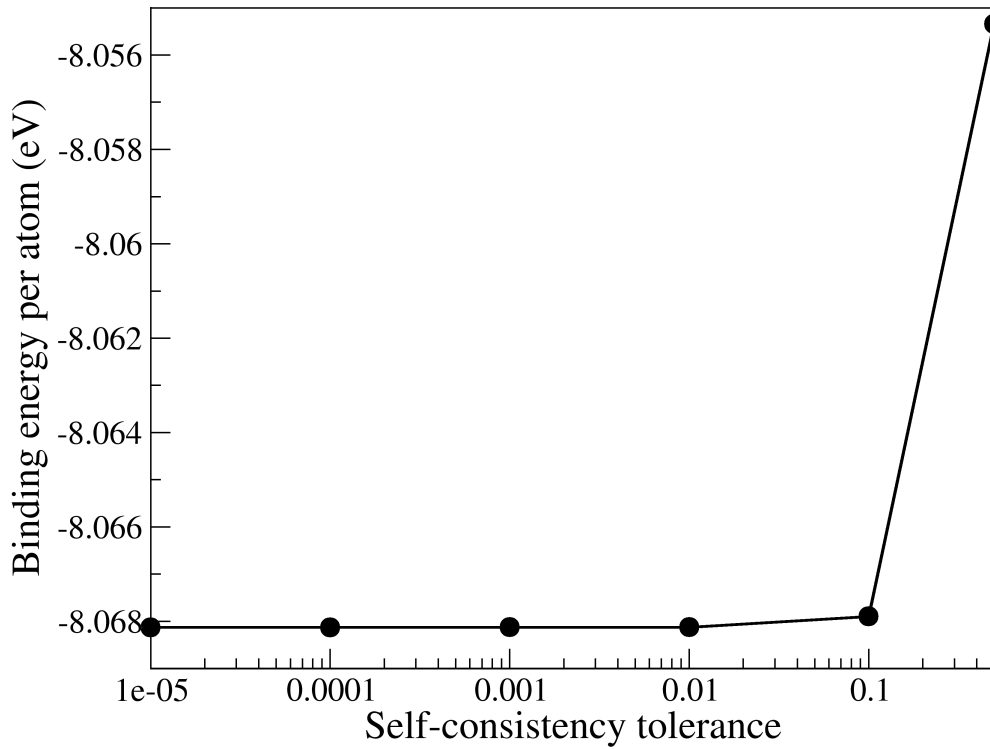


Figure 4.8: Binding energy per atom in a 2-atom FM bcc cell calculated using TB, with a  $24 \times 24 \times 24$   $k$ -point mesh, as a function of the self-consistency tolerance for the charges and magnetic moments.

minimum. Figure 4.10 shows that, as the number of moments is increased, the system does indeed tend towards the TB variational solution. However, the discrepancy between input and output magnetic moments can be as large as  $0.2 \mu_B$ , even for relatively high moment expansions. This confirms numerically that it is important to work with the gradients of the energy, rather than following the self-consistent solution to the problem, in order to remain in the ground state for a given BOP calculation.

In general, Broyden's method is able to minimise the energy very quickly in comparison with rudimentary techniques such as linear mixing. Linear mixing involves simply following the gradient downhill, always taking steps which are proportional to the gradient,

$$E'_{i\alpha\nu} = E_{i\alpha\nu} + \alpha \frac{dU_B}{dE_{i\alpha\nu}}, \quad (4.93)$$

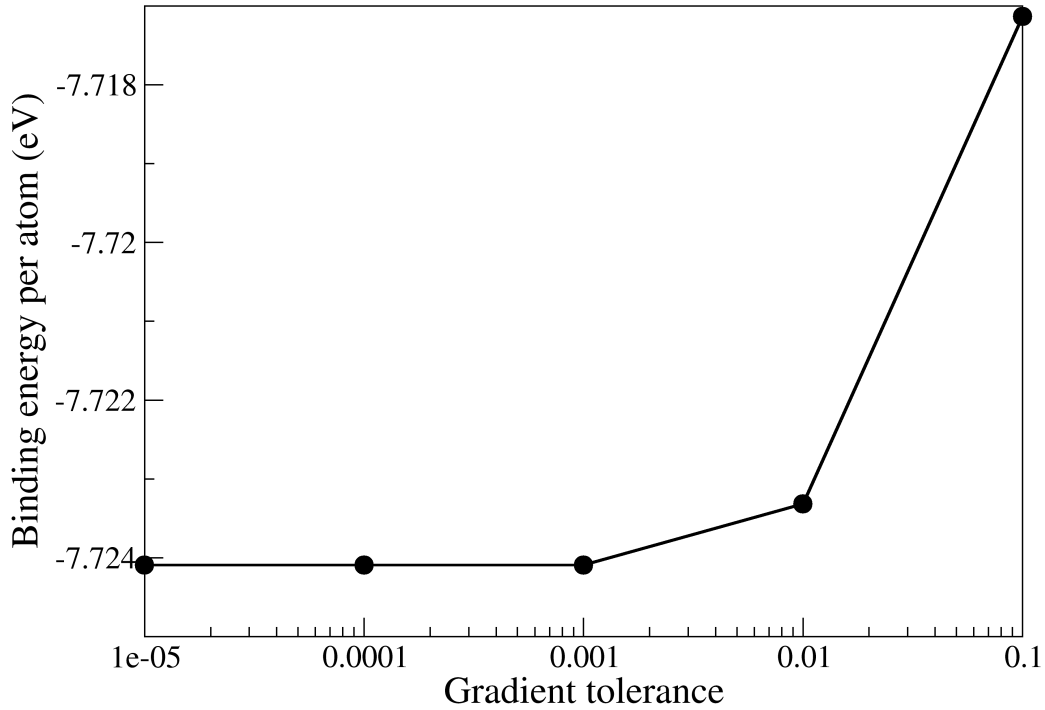


Figure 4.9: Binding energy per atom in a 2-atom AFM bcc cell calculated using 9-moment BOP as a function of the tolerance for the gradients of the energy with respect to the onsite levels.

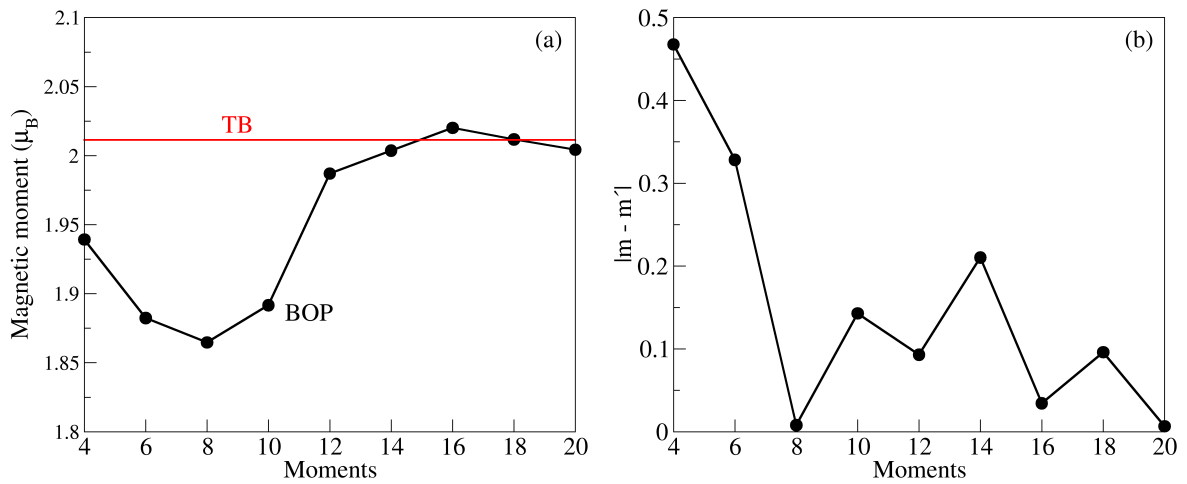


Figure 4.10: (a) Magnetic moment at local energetic minimum as a function of BOP moments calculated for a 2-atom AFM bcc cell. (b) Corresponding difference between input magnetic moments (derived from onsite level splitting) and output magnetic moments (calculated from BOP expansion) at energy minimum for each calculation in (a).

where the inverse of the Jacobian has been replaced by  $\alpha$ , now a constant. In Fig. 4.11, it can be seen that the local minimum energy is reached much more quickly with Broyden than with linear mixing. Even for  $\alpha = 0.5$ , the linear convergence is relatively slow. However, in some more complex situations, for example when a shallow local minimum is sought or when a large value of  $J_i$  required to maintain charge neutrality leads to problematically large gradients, the linear mixing method can be a safer choice to ensure the minimum is eventually reached.

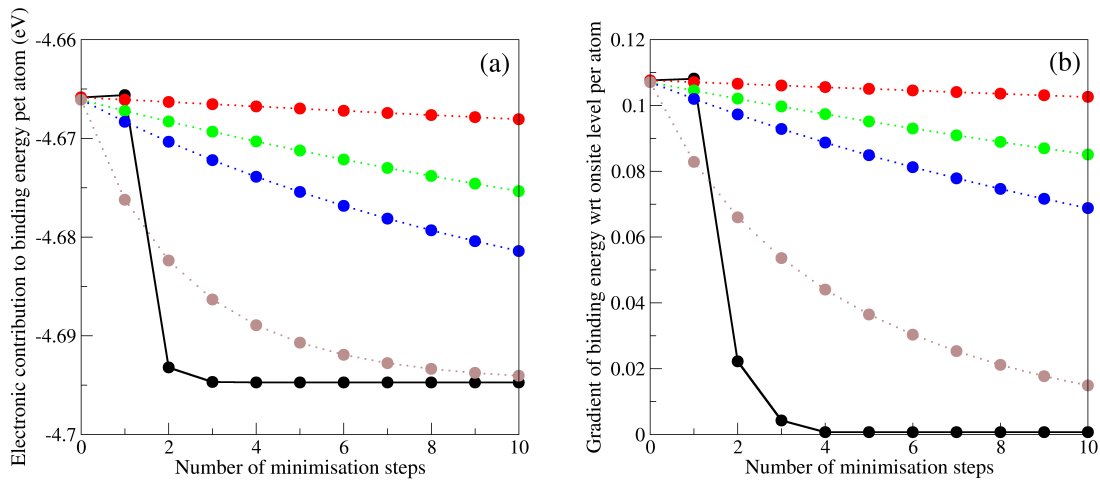


Figure 4.11: Convergence properties of the Broyden (full black) and linear mixing (dashed lines) methods tested for a FM bcc unit cell with arbitrary initial magnetic moment. The electronic contribution to the binding energy is plotted in (a), and the maximum gradient of the energy with respect to the onsite levels is plotted in (b). The colour-coding of the linear curves corresponds to  $\alpha = 0.01$  (red),  $\alpha = 0.05$  (green),  $\alpha = 0.1$  (blue), and  $\alpha = 0.5$  (brown). Larger values of  $\alpha$  lead to instabilities with the linear mixer.

## 4.5 Summary

The analytic BOP method for collinear magnetism<sup>17</sup> has been implemented into a simulation package for the first time, allowing full testing of the convergence properties as compared to exact TB calculations. The specific BOP derivatives required for the calculation of the gradients of the energy were derived and implemented, necessary for the minimisation of the energy and the calculation of forces which are consistent with that

energy. A state of local charge neutrality can be enforced numerically by adding a charge-dependent term to the binding energy, rather than the self-consistent procedure of TB.

The effect of varying the asymptotic recursion coefficients,  $a^{(\infty)}$  and  $b^{(\infty)}$ , on the BOP expansion was studied, particularly with the goal of minimising regions of negative DOS while maintaining the analytic form and computational efficiency of the BOP. A simple averaging method has been proposed, which can be derived from the linearized expansion coefficients. The hybrid analytic BOP+ method including the damping factors of the Kernel Polynomial Method has also been tested in order to remove completely the possibility of negative densities of states arising from the BOP polynomial expansion. Higher-order moments are approximated using a recursive formula to replace information in the DOS smeared out by the damping factors. This also requires a new approximation for  $a^{(\infty)}$  and  $b^{(\infty)}$ .

# Chapter 5

## Magnetic analytic BOP: applications

### I

#### 5.1 Introduction

The analytic BOP methods for collinear magnetism, both with and without the damping factors of the Kernel Polynomial Method, as described in chapter 4 are applied using a particular TB parametrisation for bulk iron. BOP results are compared to DFT and TB reference data for the energies and magnetic moments of various magnetic bulk structures, as well as the Bain structural transformation and the predicted elastic constants.

#### 5.2 Model parameters

The goal of this project was to evaluate how well the analytic BOP method could reproduce the results of TB calculations for a given parametrisation; it was not to develop an entirely new BOP parametrisation in itself. With this goal in mind, the choice of TB model was not particularly important so long as it was  $d$  electron only and orthogonal. The original choice of model was that by Liu *et al.*,<sup>114</sup> which had been shown previously to reproduce the bulk DFT structural energy differences and provide reasonable predic-

tions for the elastic constants, as well as vacancy and SIA formation energies. However, it was not possible to reproduce the TB results published in Ref. [17] with the BOPFOX code. One possible difference between the two sets of calculations was the method chosen for the  $k$ -space integration. BOPFOX uses the accurate tetrahedron method whereas the OXON code used by Liu *et al.* makes use of the Methfessel-Paxton method<sup>136</sup> where the singularities of the DOS are smeared out. In practice, the two methods should lead to the same result if the Methfessel-Paxton calculations are properly converged with respect to the smearing factor. Slightly different magnetic solutions might, however, be found as the precise value of the self-consistent magnetic moment is sensitive to the detailed structure of the DOS. It was decided *not* to base the analytic BOP tests on the Liu *et al.* model for this reason of irreproducibility. A recent publication by Soin *et al.*<sup>115</sup> also found they could not reproduce the Liu *et al.* results, attributing the differences to a lack of  $k$ -point convergence in the original paper.

A magnetic  $d$  electron orthogonal TB model for iron has instead been provided by collaborators Madsen *et al.*<sup>101</sup> at the Interdisciplinary Centre for Advanced Materials Simulation (ICAMS) in Germany. This parametrisation has also been shown to reproduce the bulk structural energy differences as well as the vacancy formation energy. The model uses bond integrals which decay exponentially with distance,

$$\beta_{\text{dd}\lambda}(r) = A_{\text{dd}\lambda} \exp(-B_{\text{dd}\lambda}r), \quad (5.1)$$

where  $\lambda$  labels the  $\sigma$ ,  $\pi$  or  $\delta$  bond contributions, and  $A_{\text{dd}\lambda}$  and  $B_{\text{dd}\lambda}$  are parameters determined by a projection from DFT. The repulsive energy is written as the sum of a pairwise repulsive term,

$$U_{\text{Rep}} = \sum_{i,j} A_{\text{Rep}} \exp(-B_{\text{Rep}}r_{ij}), \quad (5.2)$$

and an embedding energy included to approximate the neglected contribution from  $s$ - $d$

hybridisation,

$$U_{\text{Emb}} = - \sum_i \left[ \sum_{j \neq i} A_{\text{Emb}}^2 \exp(-B_{\text{Emb}} r_{ij}^2) \right]^{\frac{1}{2}}, \quad (5.3)$$

where the  $A_{\text{Rep}}$ ,  $B_{\text{Rep}}$ ,  $A_{\text{Emb}}$  and  $B_{\text{Emb}}$  are fitting parameters. The bond integrals and repulsive contributions to the energy are cut off using the following function which interpolates between 1 at a distance  $r < r_{\text{cut}} - d_{\text{cut}}$  and 0 at  $r \geq r_{\text{cut}}$ ,

$$f_{\text{cut}}(r) = \frac{1}{2} \left( \cos \left( \pi \left[ \frac{r - (r_{\text{cut}} - d_{\text{cut}})}{d_{\text{cut}}} \right] \right) + 1 \right). \quad (5.4)$$

The values of the fitting parameters and cutoffs match those used in Ref. [101] and are reproduced in Table 5.1. The resultant distance dependence of the bond integrals and repulsive functions are shown in Fig. 5.1. The number of  $d$  electrons,  $N_d$ , was set at 6.8 to fix the difference in energies between the non-magnetic fcc and hcp structures at equilibrium volume. A value of 0.76 eV for the Stoner parameter gave a good energetic separation between the magnetic and non-magnetic bcc and fcc structures. The model has a tendency to overestimate the magnitudes of magnetic moments.<sup>101</sup>

|            | A (eV)  | B ( $\text{\AA}^{-1}$ ) |      | $r_{\text{cut}}$ ( $\text{\AA}$ ) | $d_{\text{cut}}$ ( $\text{\AA}$ ) |
|------------|---------|-------------------------|------|-----------------------------------|-----------------------------------|
| $dd\sigma$ | -34.811 | 1.625                   | Bond | 3.5                               | 0.5                               |
| $dd\pi$    | 63.512  | 2.014                   | Rep  | 5.5                               | 0.5                               |
| $dd\delta$ | -50.625 | 2.597                   |      |                                   |                                   |
| Rep        | 1031    | 3.250                   |      |                                   |                                   |
| Emb        | -3.7    | 0.2230                  |      |                                   |                                   |

Table 5.1: Bond, repulsive and cut-off parameters for the Madsen *et al.* TB model.<sup>101</sup>

An alternative would have been to use the parametrisation by Mrovec *et al.*<sup>77</sup> These parameters have, however, been fitted specifically for a 9-moment numerical BOP computation and have not been tested in the literature for exact TB calculations.

Throughout the following sections the TB and BOP results are compared to DFT and EAM results. It must be remembered that the EAM potentials have been fitted to reproduce these specific phenomena. The main comparison is between the BOP and

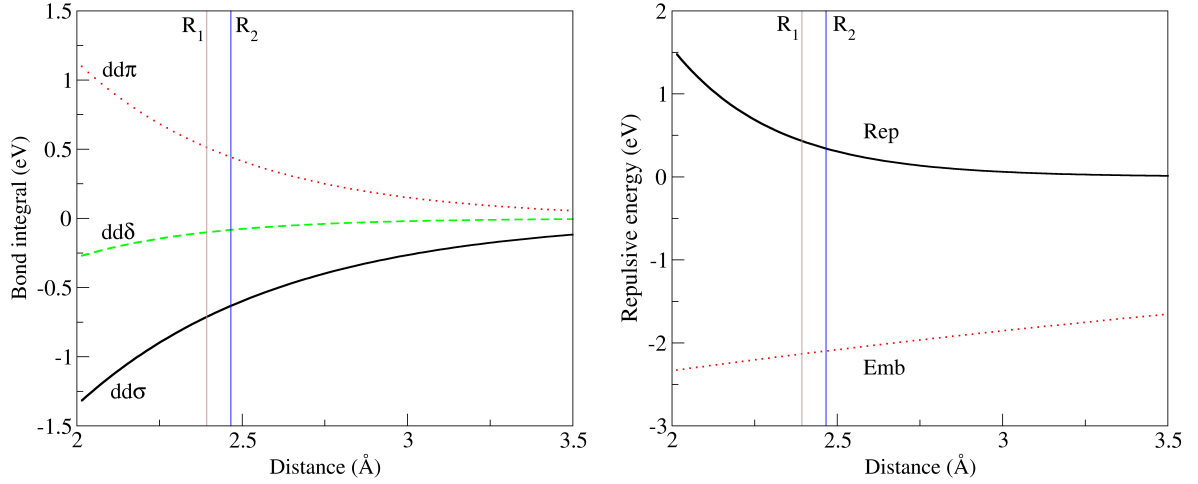


Figure 5.1: Interatomic distance dependence of the bond integral, repulsive, and embedding functions plotted for the Madsen *et al.* TB parameters.<sup>101</sup> The equilibrium nearest neighbour distances are marked as  $R_1$  for NM bcc iron and  $R_2$  for FM bcc iron.

TB methods, since these make use of the same parametrisation. It is found that BOP provides a good approximation to a given TB model. In fact, it has become clear that, in several cases, it is the TB parametrisation itself which must be improved if realistic large-scale BOP simulations of iron are to become possible. In some cases the TB model fails to reproduce what is seen at the level of DFT.

## 5.3 Bulk Fe

### 5.3.1 The density of states

The ninth moment BOP DOS for iron in the three common non-magnetic metallic crystal structures bcc, fcc and hcp are compared with DFT and TB results in Figures 5.2, 5.3 and 5.4 respectively. The first-order Methfessel-Paxton method<sup>136</sup> with a smearing of 0.1 eV was used to smooth out some of the irregularities in the TB DOS for a clearer comparison with BOP. The DOS are calculated for the same volume per atom with each method and the Fermi level is taken as the zero of the energy scale.

The DFT bcc DOS shows a large peak at the Fermi level, falling off steeply on either

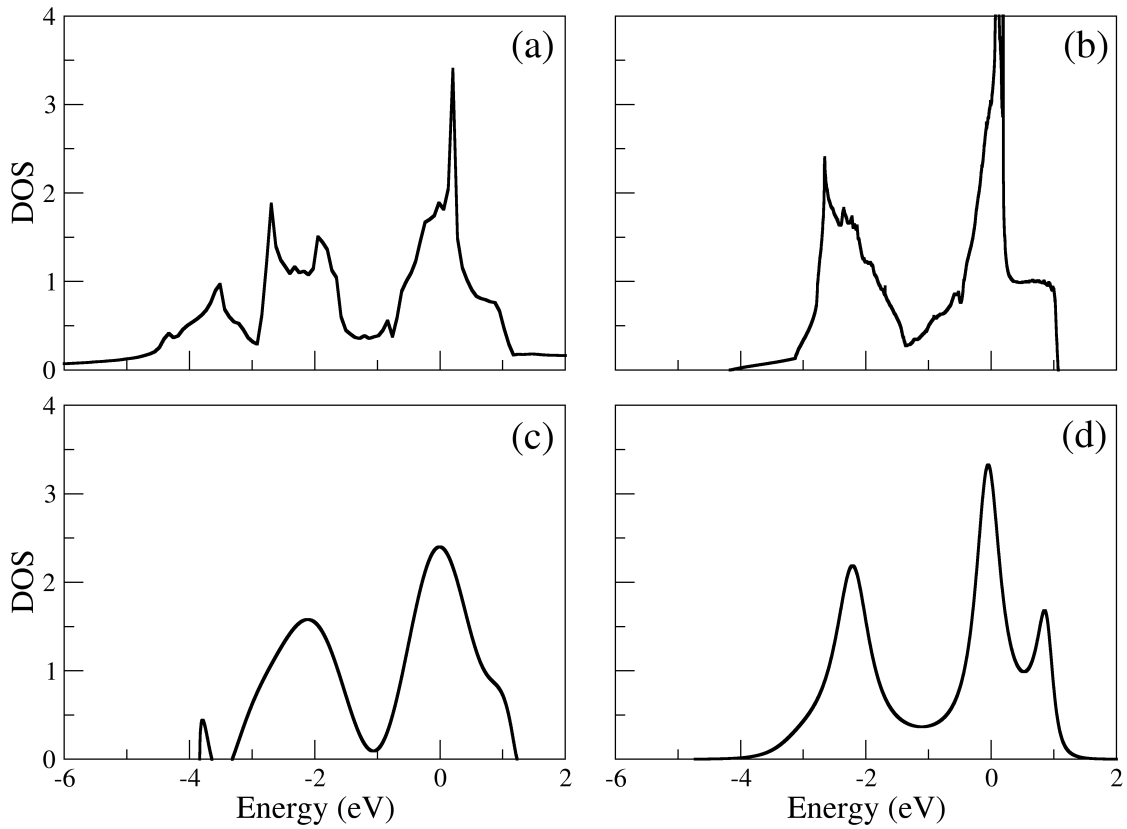


Figure 5.2: Non-magnetic bcc DOS for iron calculated at the same volume per atom with (a) DFT, (b) TB integrated using the Methfessel-Paxton method with a smearing of 0.1 eV to show the similarities between the TB and BOP, (c) 9-moment BOP with averaged  $a^{(\infty)}$  and  $b^{(\infty)}$ , and (d) 9-moment BOP+.

side, which is responsible for the stability of ferromagnetic bcc within the Stoner theory.<sup>37</sup> The  $d$  band only TB reproduces many of the features of the DFT DOS such as the sharp peak at  $E_F$ , the shoulder at higher energies and the bimodality of the distribution with a pseudogap at around -1 eV. At the level of 9 moments, the analytic BOP (using the running averaged definitions of  $a^{(\infty)}$  and  $b^{(\infty)}$ , Eqn. (4.73) and (4.74)) is able to pick up both the bimodal nature and the large peak at  $E_F$ , although there is a small region of negative DOS at the lower band edge. Combining the analytic BOP with the damping factors of the Jackson kernel and using an additional 250 fictitious moments ensures that the 9-moment DOS remains positive throughout. The peak height at the Fermi level is

also increased.

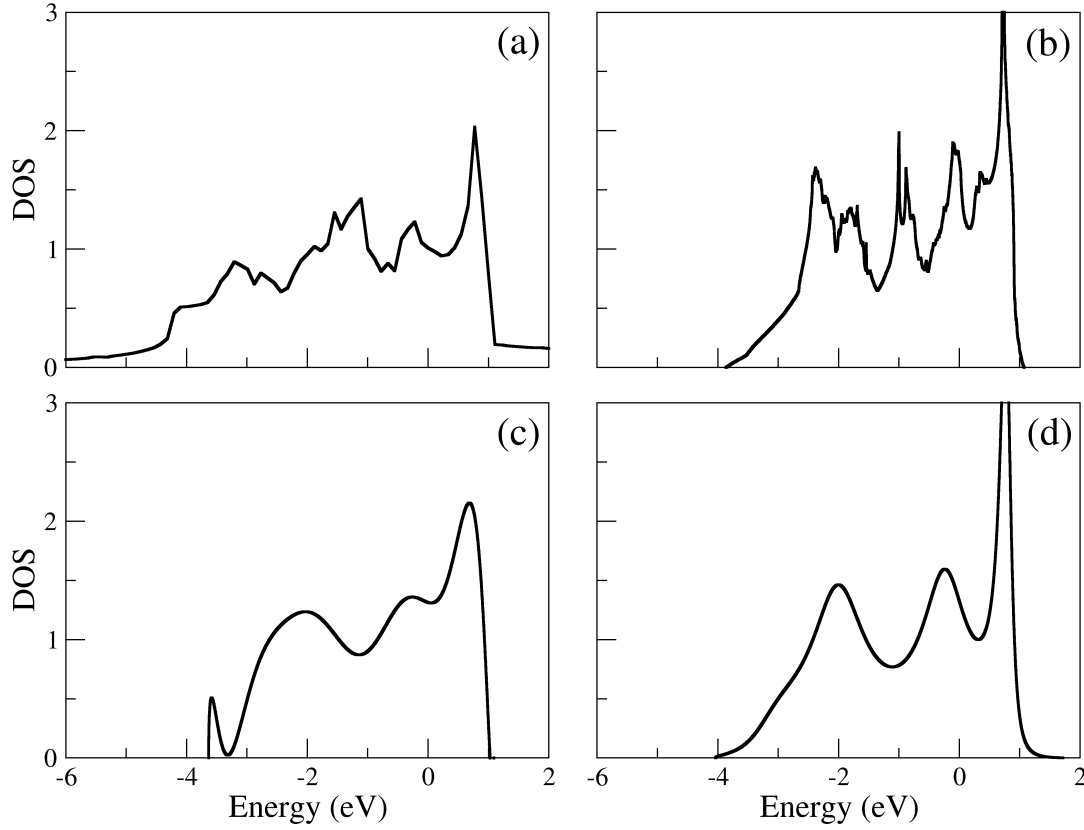


Figure 5.3: Non-magnetic fcc DOS for iron calculated at the same volume per atom with (a) DFT, (b) TB integrated using the Methfessel-Paxton method with a smearing of 0.1 eV to show the similarities between the TB and BOP, (c) 9-moment BOP with averaged  $a^{(\infty)}$  and  $b^{(\infty)}$ , and (d) 9-moment BOP+.

The features of the DFT fcc and hcp DOS are more difficult to pick out. Neither structure shows a strong peak at  $E_F$ , which in fact lies in a wide trough of the hcp distribution. The  $d$ -only TB model DOS is again similar to that of DFT, with fcc showing a weak peak at  $E_F$  and hcp a trough, although the detail is not reproduced so well. Since the band-filling dependence of the energy will be different, it is to be expected that there will be differences in the magnetic behaviour of the two structures in TB and DFT. The details of the DOS are smeared out even more by the 9-moment BOP level. Without the damping factors, both DOS display small negative regions at the lower band-edges, and

oscillations throughout the band distort the shape of the DOS at the Fermi level. For hcp the local trough is not resolved. Applying the damping factors again removes the negative region and appears to have the added benefit of improving the local shape of the DOS at  $E_F$  in both structures.

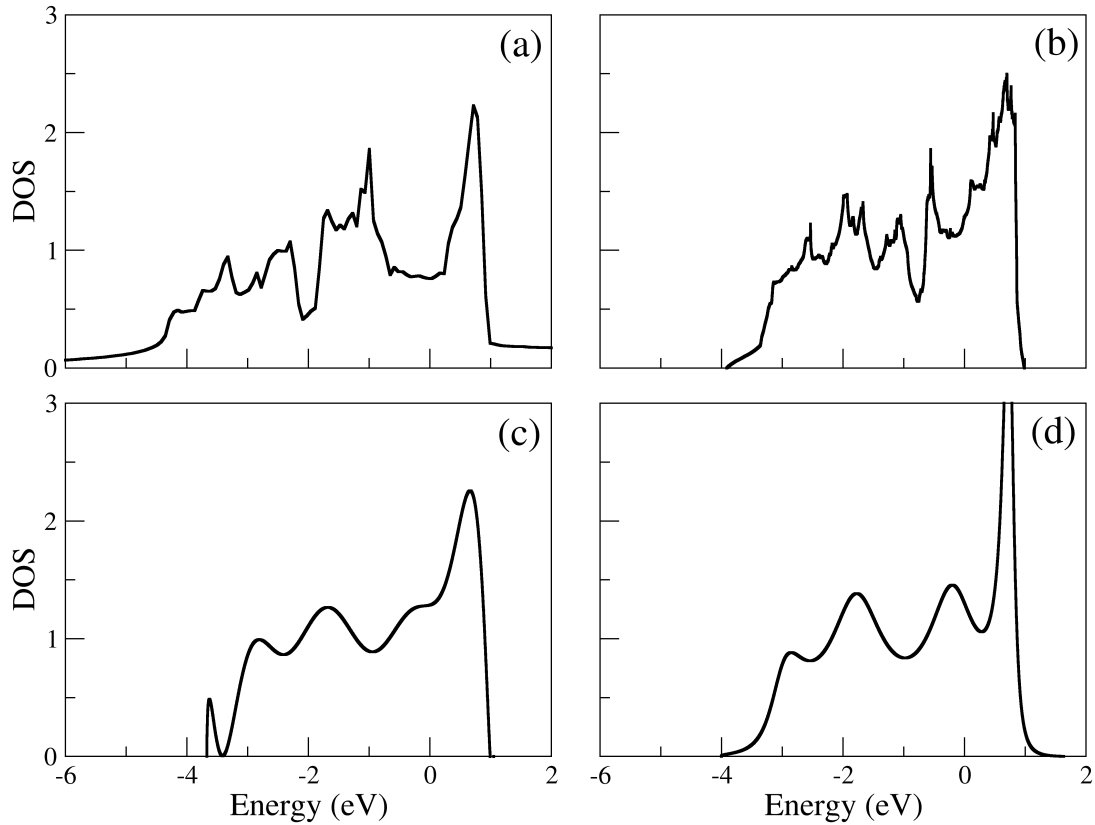


Figure 5.4: Non-magnetic hcp DOS for iron calculated at the same volume per atom with (a) DFT, (b) TB integrated using the Methfessel-Paxton method with a smearing of 0.1 eV to show the similarities between the TB and BOP, (c) 9-moment BOP with averaged  $a^{(\infty)}$  and  $b^{(\infty)}$ , and (d) 9-moment BOP with the Jackson kernel and 250 fictitious moments.

The evolution of the bcc DOS with increasing numbers of moments in the BOP expansion is illustrated in Fig. 5.5. As the number of moments is increased, the basic BOP DOS develops more and more negative regions. While these may not affect the calculation of the energy for a non-magnetic structure, the negative regions can cause severe problems during the energy minimisation in a magnetic calculation. If the mixer for some reason

causes the Fermi level to lie in a region of negative DOS, the gradients calculated will be unphysical and the calculation will, in practice, diverge. With BOP+ the DOS remains positive as the shape evolves with increasing numbers of exact moments. The development of sharp peaks at the upper band-edge is an indication of the Gibbs ringing phenomenon at what is a rather square-shaped edge of the TB DOS. This possibly indicates that the choice of bandwidth was slightly too small.

### 5.3.2 Energy and magnetisation as a function of volume

Mrovec *et al.*<sup>77</sup> have found previously that 9 moments are sufficient to provide a good reproduction of the TB energetic results for a range of structures within their numerical BOP model. In Fig. 5.6, the differences in bond energy between non-magnetic bcc and hcp, and non-magnetic fcc and hcp, are compared as a function of the number of moments using the analytic BOP method. The energy difference between two different structure types can be determined to first order, according to the structural energy difference theorem,<sup>137</sup> by the difference in electronic energies (in this case the sum of the bond and magnetic energies) when the atomic volume of each structure is adjusted to achieve the same repulsive energy per atom. hcp is taken as the reference, given that it is the non-magnetic ground state structure for Fe. The hcp/fcc difference converges quickly and at 9 moments the bcc/hcp difference is at 85% of the TB value. However, the true magnetic ground state of Fe is ferromagnetic bcc and we find that the energy of this structure is converged to within 2% of the TB energy by 9 moments, as can be seen in part (b) of Fig. 5.6. We find that 9 moments are indeed sufficient within the analytic BOP and BOP+ approximations to reproduce the TB trends in bulk structural binding energies.

The relative binding energies for the bcc, fcc and hcp structures, as calculated by DFT, TB, 9-moment BOP and 9-moment BOP+, are plotted as a function of atomic volume in Fig. 5.7. The TB reference calculations follow DFT in that the ground state structure

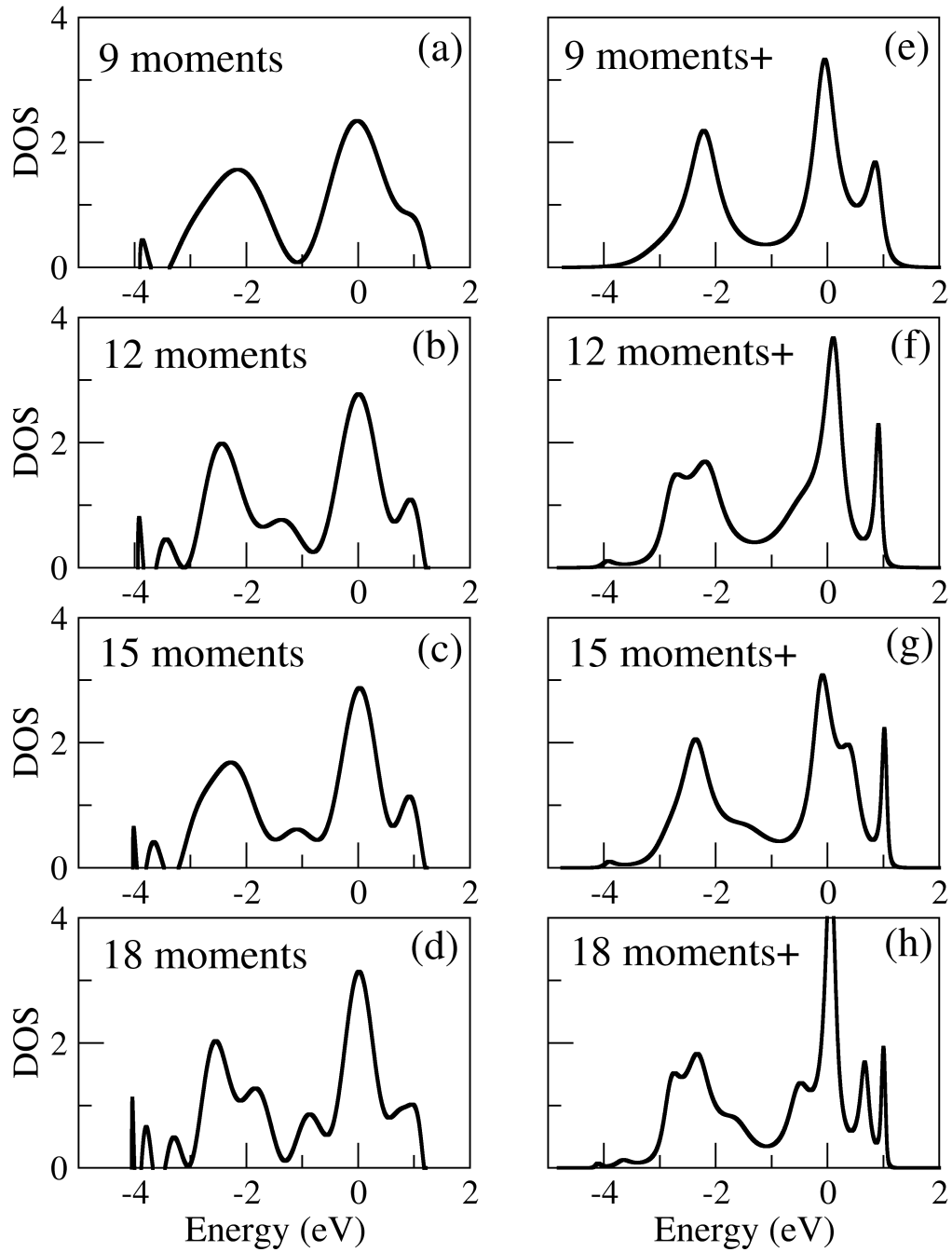


Figure 5.5: Comparison of non-magnetic bcc iron DOS calculated with BOP with (a) 9 moments, (b) 12 moments, (c) 15 moments and (d) 18 moments, and BOP+ with (e) 9 exact moments, (f) 12 exact moments, (g) 15 exact moments, and (h) 18 exact moments.

is ferromagnetic bcc, stabilised over non-magnetic bcc by 0.41 eV/atom in TB compared to 0.47 eV/atom with DFT. The general magnetic behaviour of the three structures

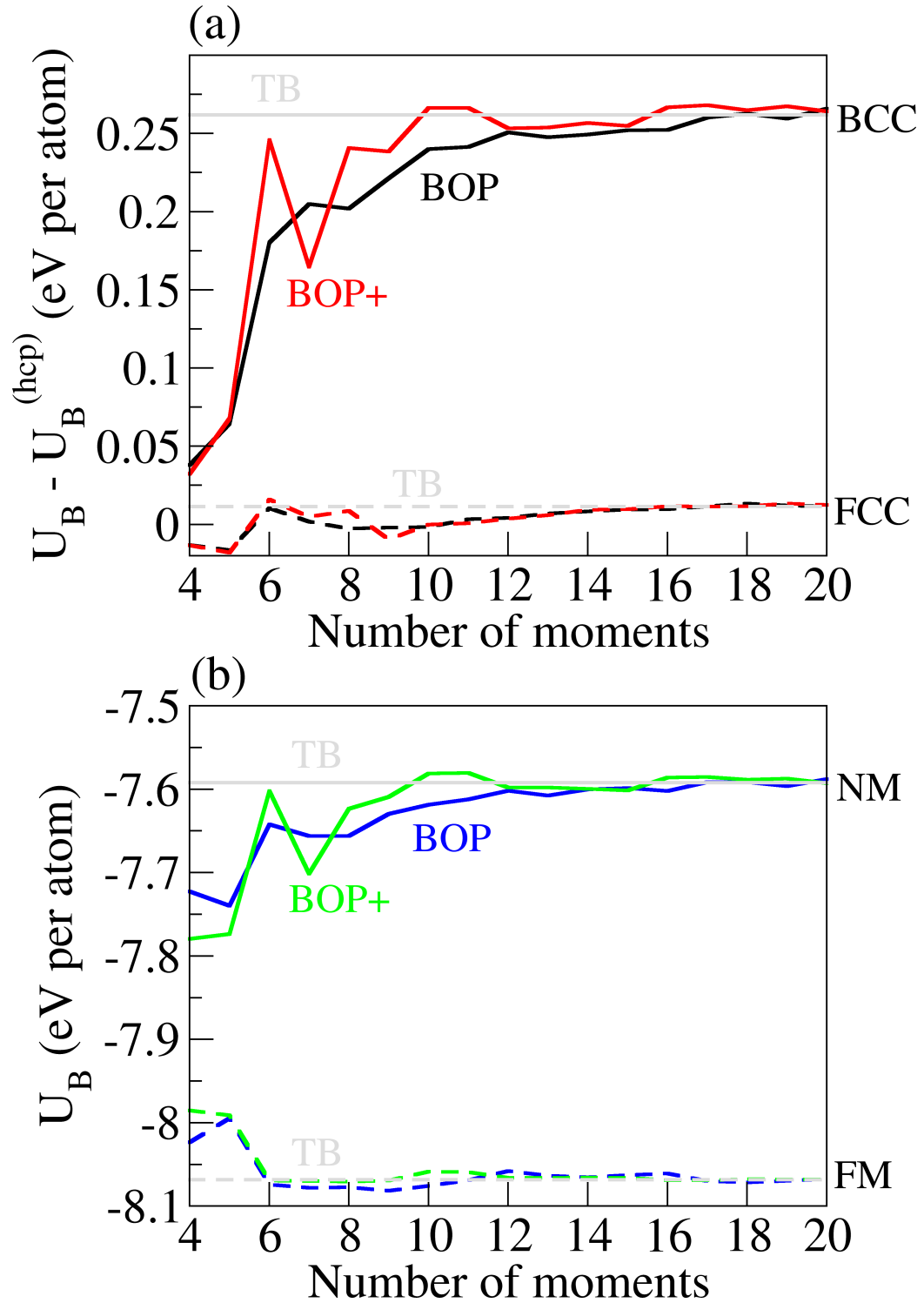


Figure 5.6: (a) Structural energy differences between non-magnetic hcp/bcc (full line) and hcp/fcc (dashed line) plotted as a function of number of exact moments in analytic BOP (black) and BOP+ (red). (b) Comparison of analytic BOP (blue) and BOP+ (green) binding energies as a function of the number of moments for non-magnetic (full lines) and FM (dashed line) bcc Fe. Corresponding TB values are marked in grey.

is similar between DFT and TB, except that the TB model significantly overstabilises antiferromagnetic hcp. This must be driven by the poor shape of the TB DOS in the region of the Fermi level, leading to an incorrect magnetic configuration (see Fig 5.9).

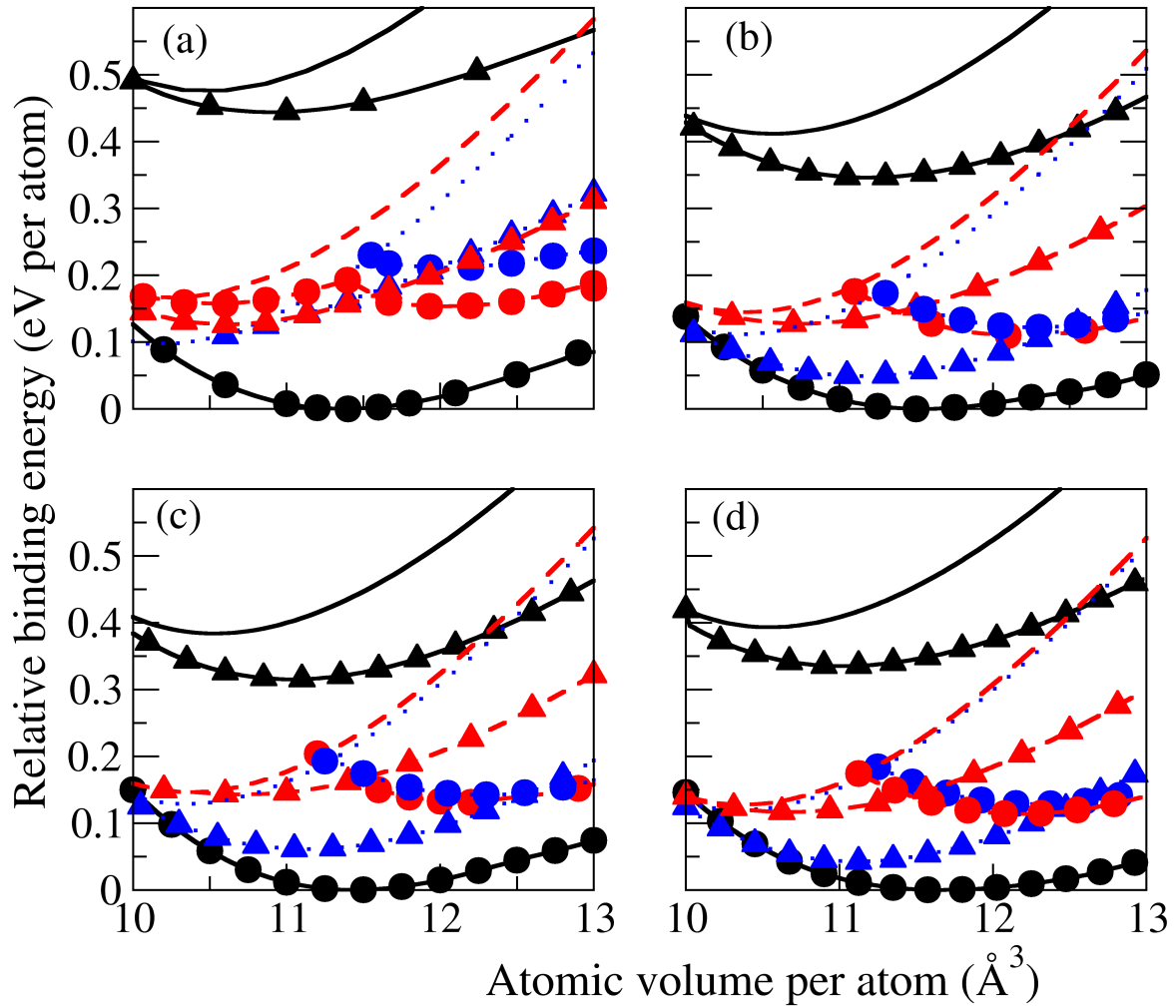


Figure 5.7: Binding energies as function of atomic volume for bcc, fcc and hcp Fe relative to the ferromagnetic bcc ground state calculated using (a) DFT, (b) TB, (c) BOP with 9 moments, and (d) BOP+ with 9 moments. Ferromagnetic configurations are marked with filled circles, antiferromagnetic with triangles and non-magnetic curves are left plain, with bcc in full black, hcp in dotted blue and fcc in dashed red.

The BOP results show the same qualitative structural trends as TB. With 9 moments, the transition volumes and energies are shifted only by small amounts and the magnetic energy contribution to ferromagnetic bcc is quantitatively accurate in comparison to TB

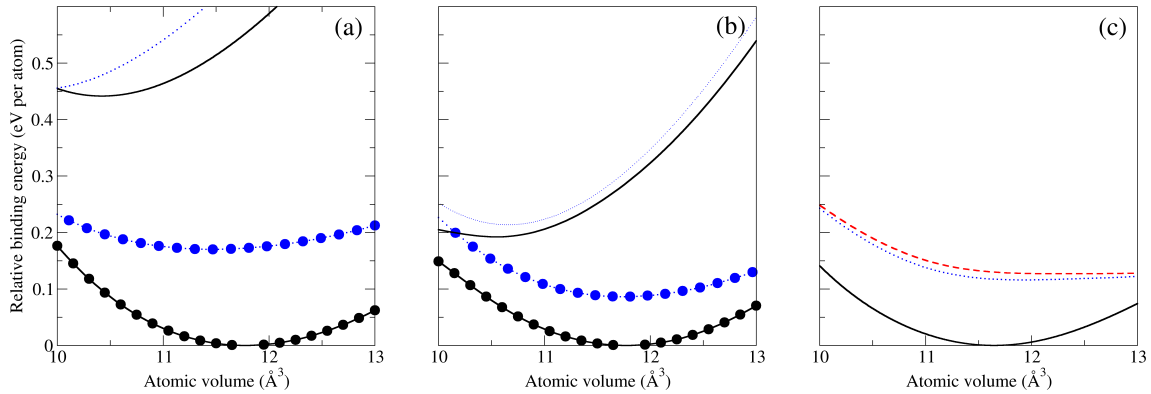


Figure 5.8: Binding energies as function of atomic volume for bcc, fcc and hcp Fe relative to the ferromagnetic bcc ground state calculated using (a) Dudarev & Derlet's<sup>8</sup> magnetic EAM model Case I, (b) Dudarev & Derlet's magnetic EAM model Case II, and (c) Mendelev's non-magnetic EAM potential.<sup>138</sup> Ferromagnetic configurations are marked with filled circles and non-magnetic curves are left plain, with bcc in full black, hcp in dotted blue and fcc in dashed red. The fcc and hcp structures have identical energies within the Dudarev & Derlet model.

(0.38 eV/atom and 0.41 eV/atom respectively). The energetic ordering is very similar with the 9-moment BOP+. The use of the upper bound on the bandwidth defined by the recursion coefficients means that the width of the DOS is generally overestimated in comparison to TB. One consequence of this is that the ground state is shifted to higher volumes ( $11.45\text{\AA}^3$  for standard BOP compared to  $11.7\text{\AA}^3$  for BOP+). This would only be overcome by including more exact moments in the expansion.

The results of three EAM based methods are included for comparison in Fig. 5.8. All three fits provide the correct ground state structure. Case I from Dudarev & Derlet's potential<sup>8</sup> has the correct energetic separation between non-magnetic and ferromagnetic bcc, although the transition between 'magnetic' and non-magnetic fcc/hcp occurs at much too low a volume because the non-magnetic energies are too high. Their Case II model, parametrised to reproduce the SIA energetic ordering, is less successful in reproducing the bcc magnetic energy difference, although the fcc/hcp curve is brought down to more realistic energies. The Mendelev potential<sup>138</sup> is unable to account for magnetism. While the ground state is fitted to bcc, the non-magnetic fcc and hcp lines show the wrong

curvature and have much too large lattice constants. All three of these fits would be unreliable bases for modelling structural transitions.

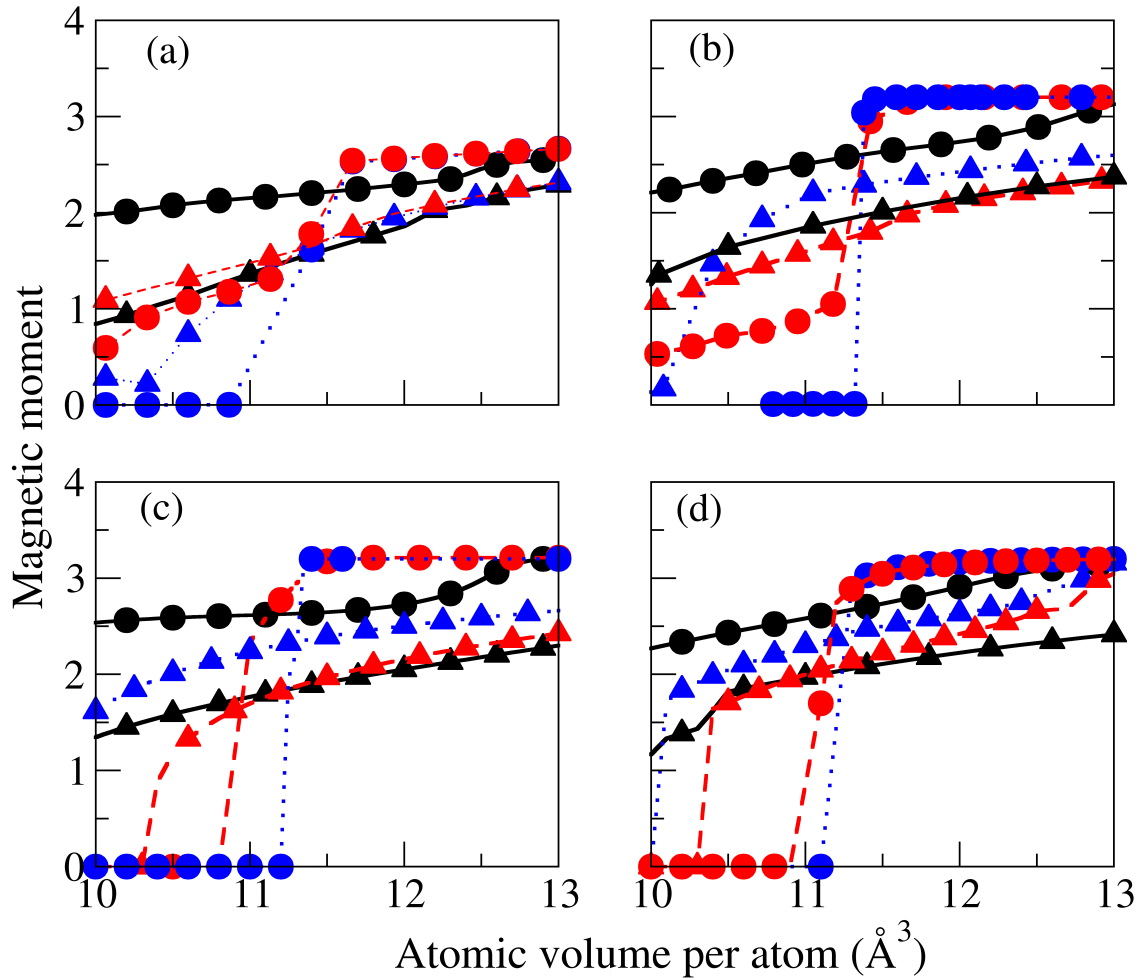


Figure 5.9: Atomic magnetic moments as function of atomic volume for bcc, fcc and hcp Fe calculated using (a) DFT, (b) TB, (c) BOP with 9 moments, and (d) BOP+ with 9 moments. Ferromagnetic configurations are marked with filled circles and antiferromagnetic with triangles, with bcc in full black, hcp in dotted blue and fcc in dashed red.

The behaviour of the magnetic moments as a function of volume is plotted in Fig. 5.9. Ferromagnetic bcc is the only configuration to retain a large magnetic moment on compression as seen in the DFT results. The moments in the close-packed structures collapse as the volume is decreased. The TB model reproduces this general behaviour. Ferromagnetic bcc sustains a large magnetic moment to low volumes while magnetism collapses in

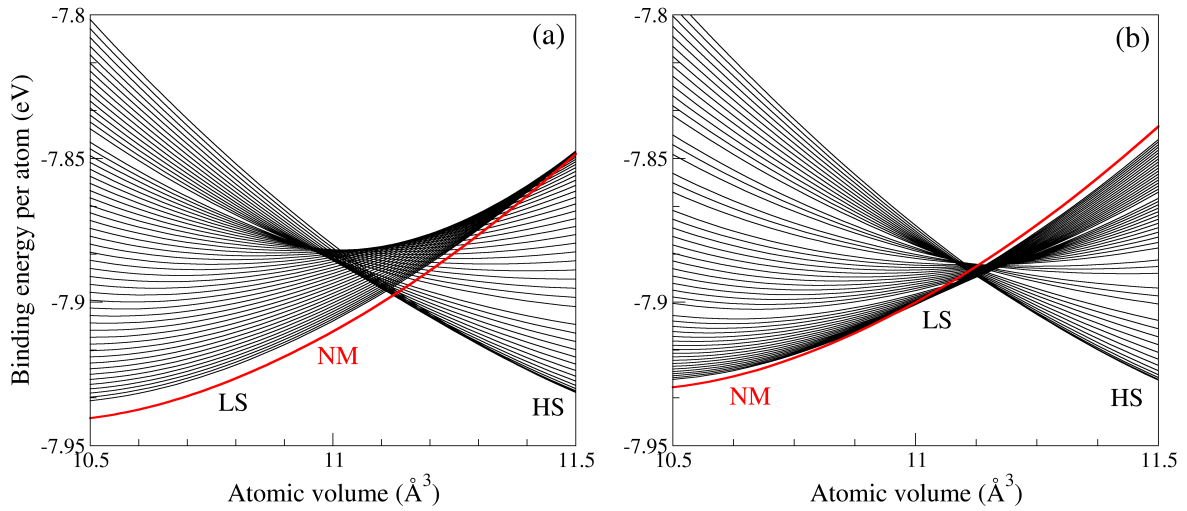


Figure 5.10: BOP+ binding energies as a function of atomic volume for fcc. Black lines mark curves of constant FM magnetic moment, while the red lines mark the non-magnetic energy. Figure (a) is calculated using 9 exact moments, figure (b) using 10. For 10 moments and above, the non-magnetic line intersects the FM curves below the LS-HS transition point.

the other structures more rapidly. The ferromagnetic hcp moment collapses precipitously while the antiferromagnetic moment decay is more gentle. The fcc and hcp structures show similar behaviour at high volumes but diverge at smaller interatomic spacings. In general, the TB model tends to overestimate the magnetic moments, particularly for ferromagnetic hcp and fcc which saturate too quickly (for a model with 6.8 electrons per atom, the maximum possible magnetic moment is  $3.2 \mu_B$ ).

The behaviour of 9-moment BOP is very similar to that of TB, except that magnetism in fcc (both ferromagnetic and antiferromagnetic) collapses more quickly on compression than predicted by the TB model. The behaviour of small magnetic moments at low volumes is determined by fine features of the DOS very near to the Fermi level, which are washed out by the BOP approximation. The agreement between BOP and TB is quantitative at higher volumes. The trends in the magnetic moments seen in the BOP+ calculations are very similar.

FM fcc in particular exhibits a low-spin (LS) to high-spin (HS) transition at a certain atomic volume, both in DFT and TB. This feature, however, is not resolved by 9-moment

BOP or BOP+. Figure 5.10 compares the energy calculated in the FM fcc structure as a function of atomic volume for fixed values of the magnetic moment. Two minima in the FM state are clearly visible. The low-volume minimum is the LS state, the high-volume minimum the HS state. For 9 moments, (a), the non-magnetic energy curve intersects the FM curves above the LS-HS transition, while for 10 moments, (b), the intersection lies below the transition point. Therefore 10 moments or more are required to detect the LS state in energy-minimised BOP calculations. Otherwise, the magnetic moment collapses to the lower-energy non-magnetic state.

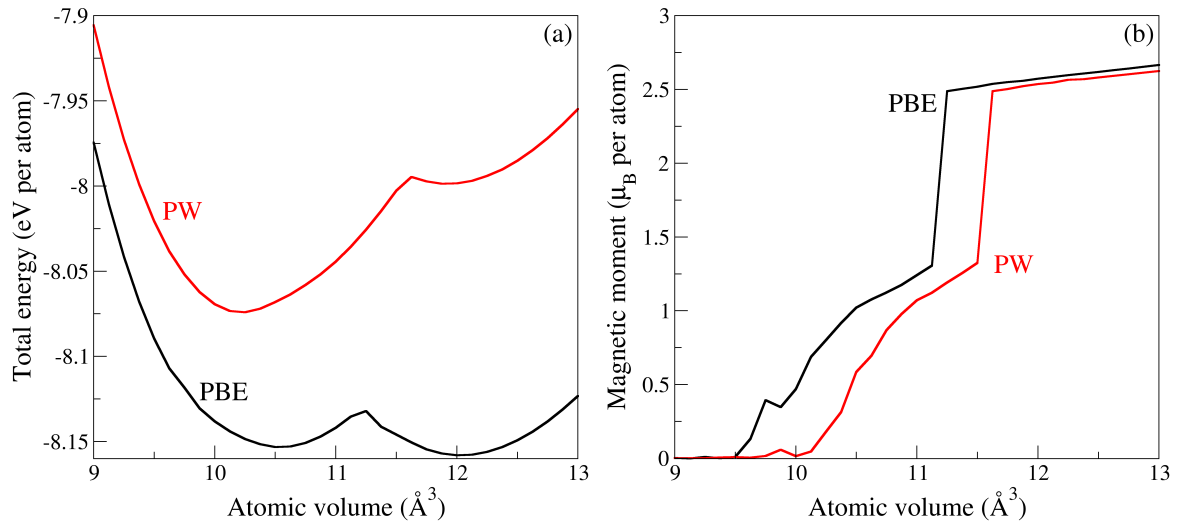


Figure 5.11: (a) Total energies and (b) magnetic moments per atom as a function of volume for FM fcc as calculated with PAW DFT using PBE (black) and PW91 (red) potentials.

The ferromagnetic moment, and hence energy, is very sensitive to the detailed structure of the fcc DOS. This sensitivity is even present in the DFT calculations. For example, while the PBE<sup>96</sup> results (from which the TB model parameters were derived) presented in Fig. 5.7 show the HS state to be lower in energy than LS, identical PAW calculations with the PW91<sup>139</sup> potential lead to a LS preference for the ferromagnetic configuration (see Fig. 5.11), consistent with the results of Herper *et al.*<sup>87</sup> The HS equilibrium atomic volume, however, matches the FM experimental result (extrapolated from precipitate studies of FM Fe-Ni, Fe-Pt and Fe-Pd)<sup>140</sup> of  $12.11 \text{ \AA}^3$  much more closely than the calculated LS

volume. This highlights yet again how difficult it is to model the itinerant magnetism in iron accurately.

### 5.3.3 The Bain transformation

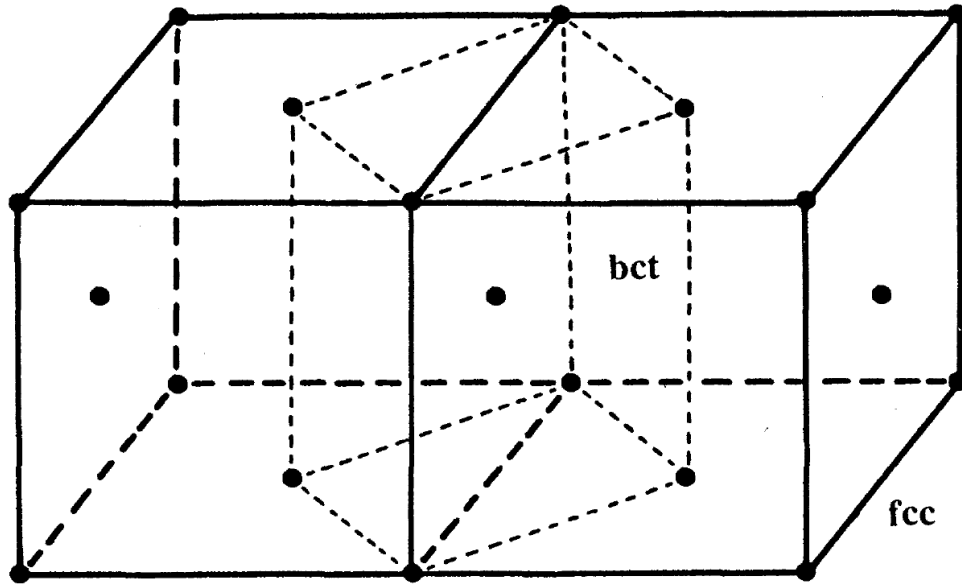


Figure 5.12: A body-centred tetragonal cell marked with dashed lines within a face-centred structure bounded by solid lines. The Bain path connects the bcc and fcc structures by varying the bct  $c/a$  ratio between 1 and  $\sqrt{2}$  respectively. Image reproduced from Ref. [141].

The relative stability of the bcc structure is investigated by plotting the energy along the tetragonal or ‘Bain’ deformation path,<sup>142</sup> whereby the unit cell  $c/a$  ratio is varied between 1 and  $\sqrt{2}$ , stretching bcc continuously into an fcc structure (see Fig. 5.12). Early Stoner calculations of the energy along the Bain path found a barrier separating local minima for ferromagnetic bcc and non-magnetic fcc at zero pressure.<sup>141</sup> The barrier height was seen to vary with pressure, only disappearing with the application of large negative pressures. Ferromagnetic fcc was found always to be mechanically unstable.

More recently full-potential DFT calculations within the GGA have shown this predicted behaviour to be incorrect.<sup>74,75</sup> At the experimental equilibrium volume of iron, ferromagnetic bcc corresponds to the global minimum of the energy while ferromagnetic

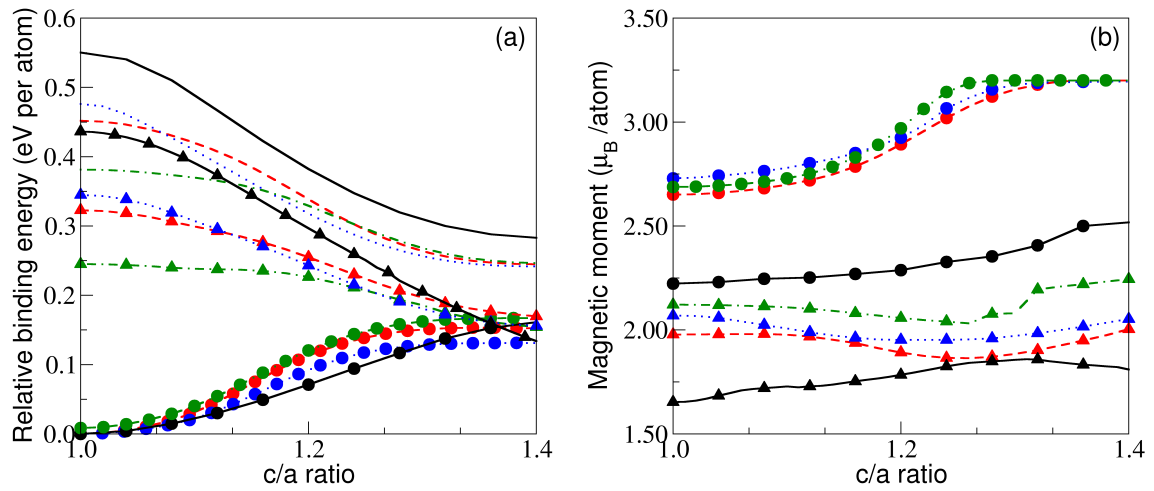


Figure 5.13: (a) Binding energies per atom relative to the ground state plotted along the tetragonal deformation path as calculated with DFT (plain black), TB (dotted blue), 9-moment BOP (dashed red) and 9-moment BOP+ (dotted and dashed green). Ferromagnetic configurations are labelled with filled circles, antiferromagnetic are labelled with filled triangles and non-magnetic are left plain. A  $c/a$  ratio of 1 corresponds to bcc while  $c/a = \sqrt{2}$  corresponds to fcc. (b) The magnetic moments corresponding to each curve plotted in (a). All calculations were performed at the TB equilibrium volume ( $11.55 \text{ \AA}^3$ ).

fcc is at a maximum. Non-magnetic bcc is at a maximum and non-magnetic fcc is a local minimum with an energy greater than ferromagnetic fcc. There is no energy barrier separating bcc and fcc when only ferromagnetic and non-magnetic configurations are taken into account. Various possible antiferromagnetic configurations are found to be lower in energy than ferromagnetic fcc but do not lead to extrema of the energy at  $c/a = \sqrt{2}$  since they break the cubic symmetry of the underlying fcc lattice. Antiferromagnetic energetic minima are found for tetragonal structures with  $c/a > \sqrt{2}$ . An antiferromagnetic double-layer minimum is found to be close to the predicted non-collinear spin-spiral ground state of fcc iron. Reproduction of this deformation behaviour is important if a potential is to be used in studies of phase transitions, particularly for the martensitic transformation which involves a deformation of the bcc structure along the Bain path to a body-centred tetragonal (bct) structure.<sup>143</sup>

The relative binding energies along the Bain path are plotted in Fig. 5.13 and Fig. 5.14. All methods were compared at the TB equilibrium volume per atom. The behaviour is similar for DFT, TB and both BOP methods tested. Ferromagnetic bcc is the ground state in iron and the energy of the ferromagnetic configuration rises continuously along the transformation to fcc, accompanied by a continuous increase in the magnetic moment. At this volume the ferromagnetic fcc structure is in the HS magnetic state, and the DFT energy profile agrees with that calculated by Friák *et al.*<sup>74</sup> Ferromagnetic fcc lies at an energetic maximum along this particular path (that is to say, it is unstable with regards to a tetragonal shear deformation). Conversely, the non-magnetic bcc structure is unstable with respect to the Bain transformation and the energy decreases as  $c/a$  is varied from 1 to  $\sqrt{2}$  until the fcc minimum is reached. The energy difference between ferromagnetic and non-magnetic configurations is underestimated by TB and BOP, especially close to the bcc structure. TB and BOP both overestimate the ferromagnetic moment significantly, leading to a saturation of the moment on transformation to fcc. The VASP DFT calculations within the GGA agree with References [74] and [75], in that antiferromagnetic configurations become more stable for  $c/a$  ratios just below  $\sqrt{2}$ , with no minimum in the

energy exhibited at fcc. The overall minimum energy profile therefore shows a cusp in the energy between bcc and fcc. While the general shape of the TB antiferromagnetic curve is correct, it does not come low enough to cross the ferromagnetic state. Although the fcc structure is predicted to be mechanically unstable, within the TB model it is unstable with regards to a transformation to ferromagnetic bcc rather than antiferromagnetic bcc as predicted by DFT. 9-moment BOP closely follows the TB curve, although application of the damping factors lowers the energy significantly enough that the antiferromagnetic state again becomes more stable at high  $c/a$  ratios, a serendipitous effect of overestimating the AFM magnetic moment.

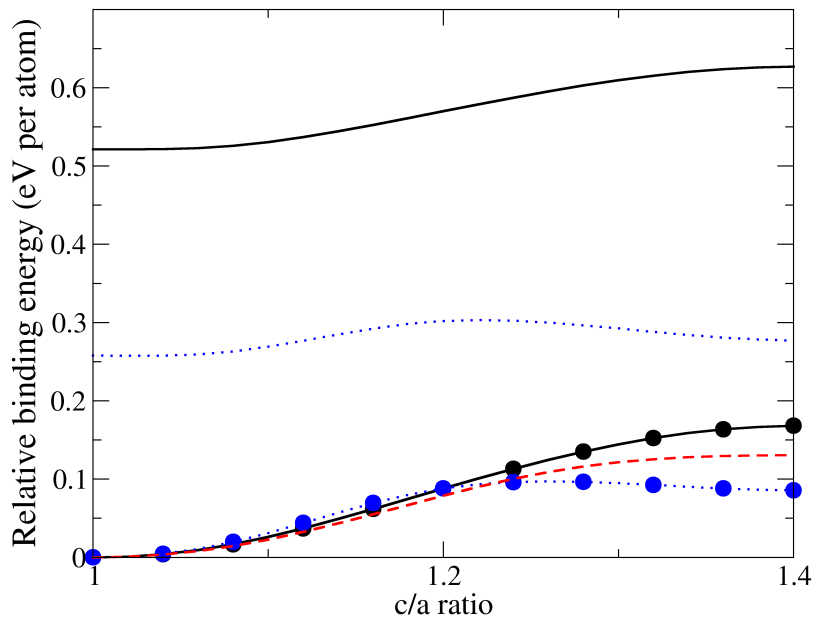


Figure 5.14: (a) Binding energies per atom relative to the ground state plotted along the tetragonal deformation path as calculated with Dudarev & Derlet's Case I potential<sup>8</sup> (plain black), their Case II potential<sup>8</sup> (dotted blue), and Mendelev's potential<sup>138</sup> (dashed red). 'Magnetic' calculations are labelled with filled circles, non-magnetic are left plain. A  $c/a$  ratio of 1 corresponds to bcc while  $c/a = \sqrt{2}$  corresponds to fcc. All calculations were performed at the TB equilibrium volume ( $11.55 \text{ \AA}^3$ ).

Dudarev & Derlet's Case I magnetic potential<sup>8</sup> and Mendelev's non-magnetic potential<sup>138</sup> both reproduce the correct behaviour of the ferromagnetic ground state. Switching

off magnetism, however, leads to qualitatively incorrect behaviour – non-magnetic bcc is found to be stable with regard to this particular transformation. Dudarev & Derlet’s Case II potential<sup>8</sup> shows incorrect behaviour for both magnetic and non-magnetic configurations. Now bcc and fcc are both found in energetic minima separated from one another by an activation barrier. The shapes of the magnetic and non-magnetic curves are similar. This behaviour is not unexpected given that Case II was fit explicitly to the SIA energetic ordering at the expense of the bulk. What is perhaps more surprising is that the potential fitted to the bulk, Case I, is only able to reproduce the *ab initio* data for the ferromagnetic configuration.

### 5.3.4 Elastic constants

The elastic constants are a further important test of an interatomic potential and may be calculated from the second derivative of the total energy with respect to distortions of the crystal along particular axes. The elastic constants,  $C_{ij}$ , relate the elastic energy and homogeneous strain in the material,

$$U_{El} = \frac{1}{2} \sum_{ij} C_{ij} \epsilon_i \epsilon_j. \quad (5.5)$$

For the cubic ground state of iron there are three independent elastic constants  $C_{11}$ ,  $C_{12}$  and  $C_{44}$ . One may also use as alternatives the bulk modulus,  $B = \frac{1}{3} (C_{11} + 2C_{12})$ , and the tetragonal shear modulus,  $C' = \frac{1}{2} (C_{11} - C_{12})$ .  $C_{44}$  is referred to as the rhombohedral shear modulus.

The three elastic constants are calculated following Ref. [83] by deforming the lattice vectors of the simulation cell according to

$$\mathbf{a}' = \mathbf{a} + \gamma \mathbf{T} \mathbf{a}, \quad (5.6)$$

where  $\gamma$  is the magnitude of the distortion and  $\mathbf{T}$  the deformation matrix which determines

the symmetry of the distortion. The particular deformation matrix for  $C_{11} + 2C_{12}$  is the identity matrix,

$$\mathbf{T}_{C_{11}+2C_{12}} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad (5.7)$$

for  $C_{11} - C_{12}$  it is

$$\mathbf{T}_{C_{11}-C_{12}} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -\frac{1}{2} & 0 \\ 0 & 0 & -\frac{1}{2} \end{pmatrix}, \quad (5.8)$$

and for  $C_{44}$  it is

$$\mathbf{T}_{C_{44}} = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}. \quad (5.9)$$

The unit cell is distorted in four steps of  $\gamma$  in either direction from equilibrium with a full relaxation of the ionic positions performed at each step. A cubic polynomial is fitted to extract the second derivative of the energy,  $\frac{d^2 U_B}{d\gamma^2}$ , such that the bulk modulus is given by

$$B = \frac{1}{9V_C} \frac{d^2 U_B}{d\gamma^2}, \quad (5.10)$$

$C'$  is given by

$$C' = \frac{1}{3V_C} \frac{d^2 U_B}{d\gamma^2}, \quad (5.11)$$

and  $C_{44}$  is given by

$$C_{44} = \frac{1}{4V_C} \frac{d^2 U_B}{d\gamma^2}, \quad (5.12)$$

where  $V_C$  is the volume of the cell.

The elastic constants for non-magnetic and ferromagnetic bcc iron as calculated with TB, 9-moment BOP and 9-moment BOP+, are compared in Table 5.2 with published DFT

|          | NM   |      |     |      | FM  |     |     |      | Exp. |
|----------|------|------|-----|------|-----|-----|-----|------|------|
|          | DFT  | TB   | BOP | BOP+ | DFT | TB  | BOP | BOP+ |      |
| $B$      | 276  | 266  | 254 | 267  | 186 | 157 | 197 | 121  | 172  |
| $C'$     | -110 | -101 | -42 | -54  | 69  | 25  | 32  | 27   | 43   |
| $C_{44}$ | 141  | -34  | 17  | -16  | 99  | 18  | 26  | 19   | 116  |

Table 5.2: Elastic constants (GPa) for non-magnetic and ferromagnetic bcc iron. BOP and BOP+ calculations included up to 9 moments. DFT results are reproduced from Ref. [144] and the room-temperature experimental results are from Ref. [145].

and experimental results. The published DFT results were calculated using the FLAPW method and the PBE GGA potential.<sup>144</sup> Both BOP methods are able to reproduce the large, positive bulk modulus seen for non-magnetic iron with the TB model. They also both lead to negative values of  $C'$ , although the absolute value is underestimated by BOP and BOP+. This negative value means that non-magnetic bcc is unstable with respect to the tetragonal distortion as was seen in section 5.3.3 by analysis of the energy along the Bain path. The BOP method is unable to reproduce the value of  $C_{44}$  at this level of approximation, with even the sign being incorrect.

The TB model reproduces the sign and relative magnitude of  $B$ , but not  $C'$  and  $C_{44}$ , as calculated for ferromagnetic iron with DFT and measured in experiment. 9-moment BOP overestimates the value of the bulk modulus, while application of the damping factors in the BOP+ leads to an underestimation.  $C'$  is positive with both methods, showing that the ferromagnetic bcc is stable with respect to the tetragonal distortion. Again, the values of  $C_{44}$  are less well reproduced.

| Moments  | 9   | 11  | 15  | 20  | Moments  | 9   | 11  | 15  | 20   |
|----------|-----|-----|-----|-----|----------|-----|-----|-----|------|
| $B$      | 254 | 250 | 250 | 249 | $B$      | 267 | 266 | 265 | 264  |
| $C'$     | -42 | -71 | -75 | -95 | $C'$     | -54 | -51 | -83 | -102 |
| $C_{44}$ | 17  | -65 | -14 | -46 | $C_{44}$ | -16 | -46 | -18 | -7   |

Table 5.3: Table on left shows the elastic constants (GPa) for non-magnetic iron calculated with 9-, 11-, 15- and 20-moment BOP. The corresponding BOP+ results are in the table on the right.

The particular TB model<sup>101</sup> does not provide a good reproduction of the DFT or experimental elastic constants, although these were not actually included in the fit of the TB parameters. More strikingly, perhaps, the BOP and BOP+ constants converge very slowly towards the equivalent TB results, except for the bulk modulus. Table 5.3 compares the values of the three constants for non-magnetic bcc iron as calculated with BOP and BOP+ using 9, 11, 15 and 20 moments. While the bulk modulus changes little with increasing moments,  $C'$  converges more slowly and 20 moments are required to come close to the TB value.  $C_{44}$  is not seen to converge to a sensible value at all. In fact, with 9 moments, the BOP  $C_{44}$  even has the wrong sign compared to TB. Table 5.4 compares the same values as calculated for the ferromagnetic bcc structure. The bulk modulus converges more slowly than for the non-magnetic state, as does  $C'$ . The variation in  $C_{44}$  is so large that the reasonably accurate value by 20 moments is simply fortuitous. The 11-moment BOP model exhibits a negative  $C_{44}$  – the groundstate of this model is clearly not exactly ferromagnetic bcc. The energy along this rhombohedral distortion path is plotted for TB and 11-moment BOP in Figure 5.15. The BOP energy is indeed lowered very slightly by distorting the bcc cell by 0.015 Å along this  $C_{44}$  path.

| Moments  | 9   | 11  | 15  | 20  | Moments  | 9   | 11  | 15  | 20  |
|----------|-----|-----|-----|-----|----------|-----|-----|-----|-----|
| $B$      | 197 | 155 | 137 | 166 | $B$      | 122 | 118 | 152 | 144 |
| $C'$     | 32  | 17  | 16  | 26  | $C'$     | 27  | 25  | 26  | 24  |
| $C_{44}$ | 26  | -25 | 11  | 26  | $C_{44}$ | 19  | 7   | 9   | 18  |

Table 5.4: Table on the left shows elastic constants (GPa) for ferromagnetic iron calculated with 9-, 11-, 15- and 20-moment BOP. The corresponding BOP+ results are in the table on the right.

The poor representation of  $C'$  and particularly  $C_{44}$  with BOP is a reflection of the generally slow convergence of forces or derivatives of the energy, which converge less quickly to the exact  $k$ -space TB reference than the bulk structural energies themselves within BOP and the recursion method.<sup>146</sup> The shear constants converge more slowly than

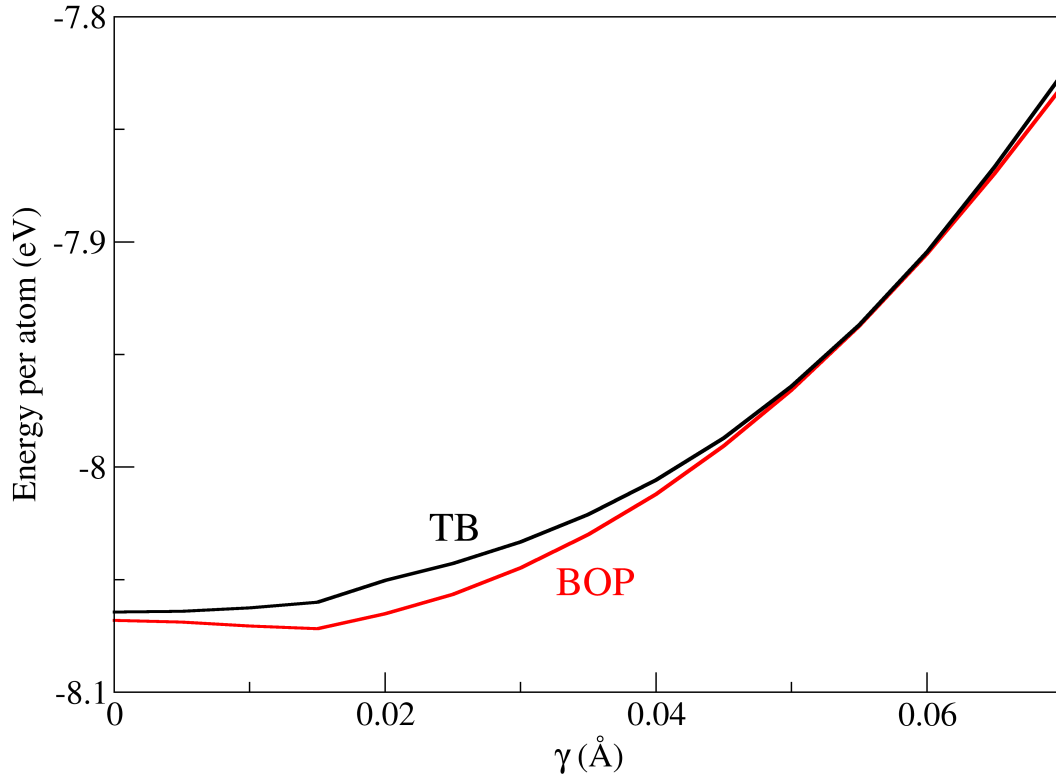


Figure 5.15: Binding energy per atom plotted along the FM bcc rhombohedral deformation path for TB and 11-moment BOP.  $\gamma$  refers to the displacement along the path according to Eqn. (5.6), with the deformation matrix,  $T$ , given by Eqn. (5.9). The BOP results show an energetic minimum at a displacement of 0.015 Å.

$B$  because they rely upon a converging cancellation between oscillating force constants going out many levels into the material. While low moment expansions can describe general shear behaviours, they have been shown previously not to be quantitative.<sup>147</sup> The shear distortions can be associated with corresponding distortions of the Fermi surface, responsible, for example, for the observed anomalies in the temperature dependence of the shear constants in Pd, Pt, V, Nb and Ta.<sup>148,149</sup> These effects are strongest for  $C_{44}$  where the distortion involves a change in the nearest neighbour distances missing from the  $C'$  distortion to first order.<sup>148</sup> In fact, recursion method calculations of the phonon spectrum of iron required a large cluster of 14911 atoms and included interactions up to

13 exact levels of the continued fraction (26 moments).<sup>150</sup> Since the BOP DOS is always smooth, even up to very high numbers of moments or recursion levels, it is unable to reproduce the necessary detailed structure near the Fermi level for an accurate prediction of these shear constants. As we have seen, this can even lead to a slightly distorted groundstate structure. A similar effect is observed in the recursion method; sharp changes in elastic constants as a function of the  $d$  band filling are not resolved because the van Hove singularities are smeared out. This is true even up to thirty moments as found by Nastar & Willaime.<sup>147</sup> A fully-functional analytic BOP model would therefore require a specific refitting of the bond parameters and repulsive function in order to reproduce the experimental elastic constants for a given number of moments in the BOP expansion. This is the approach taken for the numerical BOP for iron.<sup>77</sup>

## 5.4 Summary

The analytic BOP method (both with and without the Jackson kernel) has been compared to exact TB results using the model by Madsen *et al.*<sup>101</sup> 9 moments are found to be sufficient to reproduce the trends in many of the bulk properties of iron, including the variation of the energy and magnetic moments as a function of atomic volume. The over-stabilisation of antiferromagnetic hcp iron is a problem of the TB parametrisation also evident in the BOP calculations. 10 moments or more are required to observe the HS/LS transition in fcc iron. The BOP methods are able to reproduce the TB behaviour along the important Bain transformation path, although once again the TB results differ from the DFT reference data. The description of the elastic constants with BOP, however, is poor and many moments are required for these to converge towards the TB values, particularly the tetragonal shear modulus. An interatomic potential for realistic mechanical simulations would require a specific fitting of the elastic constants.

# Chapter 6

## Magnetic analytic BOP: applications

### II

#### 6.1 Introduction

The analytic BOP methods for collinear magnetism, both with and without the Jackson kernel, as described in chapter 4 are tested using the Madsen *et al.*<sup>101</sup> TB parametrisation for both point and planar defects in iron. BOP results are compared to DFT and TB reference data for the monovacancy and divacancy in bcc Fe, the three possible self-interstitial atom defect configurations, and the (100) bcc surface.

#### 6.2 Point defects

##### 6.2.1 Monovacancy

The monovacancy in ferromagnetic bcc iron has previously been studied with *ab initio*<sup>151</sup> and TB<sup>114</sup> methods. The defect formation energy is defined by

$$U_f^{\text{def}} = U_{\text{B}}^{\text{def}} - \frac{N^{\text{def}}}{N} U_{\text{B}}, \quad (6.1)$$

where  $N$  and  $N^{\text{def}}$  are the numbers of atoms in the perfect and defective calculation cells respectively, and  $U_{\text{B}}$  and  $U_{\text{B}}^{\text{def}}$  are the total binding energies of the two cells. The results of some published DFT, TB and experimental formation energies for the vacancy are collated in Table 6.1. The DFT values lie within the range of values determined by positron-annihilation experiments.<sup>152</sup>

| Method              | $U_{\text{un}}^{\text{vac}}$ | $U_{\text{f}}^{\text{vac}}$ | Method         | $U_{\text{un}}^{\text{vac}}$ | $U_{\text{f}}^{\text{vac}}$ |
|---------------------|------------------------------|-----------------------------|----------------|------------------------------|-----------------------------|
| DFT <sup>151</sup>  | 2.24                         | 1.95                        | DFT (PAW PBE)  | 2.37                         | 2.14                        |
| DFT <sup>153</sup>  | -                            | 1.94                        | DFT (PAW PW91) | -                            | 2.15                        |
| TB <sup>114</sup>   | 1.74                         | 1.65                        | DFT (US PBE)   | 2.23                         | 1.96                        |
| Exp. <sup>152</sup> | -                            | $2 \pm 0.2$                 | TB             | 2.01                         | 1.86                        |
|                     |                              |                             | BOP            | 2.04                         | 1.93                        |
|                     |                              |                             | BOP+           | 2.09                         | 2.02                        |

Table 6.1: Table on left shows vacancy published formation energies (in eV) in ferromagnetic bcc iron as found with DFT, TB and experimental methods. Table on right shows vacancy formation energies as calculated as part of this work with various flavours of DFT, TB, 9-moment BOP and 9-moment BOP+.  $U_{\text{un}}^{\text{vac}}$  is the unrelaxed vacancy formation energy and  $U_{\text{f}}^{\text{vac}}$  is the relaxed value. PAW and US refer to the projector augmented wave<sup>94,95</sup> and ultrasoft<sup>154</sup> pseudopotential methods, while PBE<sup>96</sup> and PW91<sup>139</sup> refer to specific GGA exchange-correlation potentials.

The formation energy of the monovacancy has also been calculated as part of this work with DFT, TB and both BOP methods using a 54-atom supercell (see Table 6.1). VASP calculations using the projector augmented wave (PAW)<sup>94,95</sup> method and the PBE<sup>96</sup> XC potential do not reproduce the most-commonly cited DFT vacancy formation energies, which have been calculated previously using the ultrasoft pseudopotential (US)<sup>154</sup> method. VASP calculations with US PBE led to a value of the relaxed vacancy formation energy of 1.96 eV, close to the published 1.95 eV<sup>151</sup> and 1.94 eV.<sup>153</sup> The PAW method, however, leads to a relaxed formation energy of 2.14 eV with PBE, or 2.15 eV with the PW91<sup>139</sup> XC potential. The  $k$ -point convergence of the defect energy calculations was slow and an  $8 \times 8 \times 8$  mesh was required for a convergence of the formation energy below 0.1 eV. A more extensive literature search uncovered one published PAW calculation for the vacancy

formation energy, 2.16 eV, using a larger (128-atom) supercell, which is consistent with these results.<sup>155</sup>

Kresse & Joubert<sup>95</sup> have already compared the US and PAW methods in detail for a range of materials. While the results of US and PAW calculations are almost identical for all elements in both atomic and bulk conditions, the US method is found to have a particular problem with describing magnetic iron within the GGA, compared to PAW and all-electron methods. For example, they found the US energy difference between non-magnetic hcp and ferromagnetic bcc structures is more than double the PAW result for the same XC potential (0.073 eV versus 0.191 eV). In a system like iron, with many competing magnetic configurations separated by small energy differences, such inaccuracies could change the relative ordering of both bulk and defect structures.

Since no systematic comparison of the PAW and US methods for the iron system has been published, the volume-dependence of the relative binding energy for the PBE PAW calculations is compared with those of PBE US calculations in Fig. 6.1. While we find non-magnetic structural energy differences to be identical, there are subtle differences between the various magnetic structures. For example, the magnetic energy of ferromagnetic bcc is 0.48 eV per atom with PAW but 0.56 eV per atom with the US method. There is a corresponding shift in the ground state volume per atom – 11.40 Å<sup>3</sup> for PAW compared to 11.65 Å<sup>3</sup> for US – which compares well to that also found by Olsson *et al.*<sup>156</sup> The transition points between structures and magnetic configurations are shifted to different volumes. The US bcc/hcp ground state transition occurs at higher pressures than for PAW, as does the ferromagnetic/antiferromagnetic hcp transition. These observations are consistent with those of Kresse & Joubert. A more detailed analysis of the differences between US and PAW calculations is not within the scope of this work, but since the PAW method is found to reproduce the results of all-electron calculations for bulk structures,<sup>95</sup> it is likely that the PAW defect energies are more accurate than those calculated with the US method and are therefore used as the reference for the TB and BOP studies presented here. This analysis does not take into account the known problems encountered with

the DFT exchange-correlation description for the evanescent electron densities at crystal surfaces, both external or internal as in the case of the vacancy.<sup>157</sup>

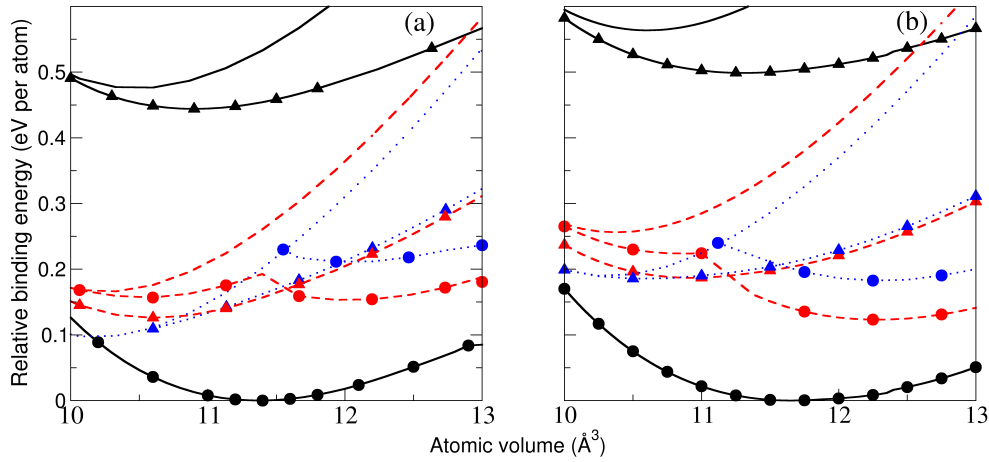


Figure 6.1: DFT PBE functional binding energies as function of atomic volume for bcc, fcc and hcp Fe relative to the ferromagnetic bcc ground state calculated using (a) the PAW methods and (b) the US method. Ferromagnetic configurations are marked with filled circles, antiferromagnetic with triangles and non-magnetic curves are left plain, with bcc in full black, hcp in dotted blue and fcc in dashed red.

The values of the TB unrelaxed and relaxed formation energies lie close to the range of the experimental data. The unrelaxed vacancy formation energy is reproduced well by BOP with 9 moments, while the discrepancy in the relaxed energy is slightly larger at 4.6%. Application of the damping factors only leads to small changes in the formation energies.

For comparison, the vacancy formation energies as calculated by EAM methods are presented in Table 6.2. All three models generate formation energies in line with experiment, although these are achieved by including the DFT vacancy energy directly in the fitting database.

The atomic shell relaxations about the vacancy are shown in Fig. 6.2. The behaviour is similar in both DFT and TB; the nearest neighbours relax strongly towards the vacancy while the displacements of subsequent layers alternate. 9-moment BOP picks up the TB

| Method        | $U_{\text{un}}^{\text{vac}}$ | $U_{\text{f}}^{\text{vac}}$ |
|---------------|------------------------------|-----------------------------|
| D & D Case I  | 2.25                         | 2.07                        |
| D & D Case II | 2.07                         | 1.98                        |
| Mendelev      | 1.87                         | 1.72                        |

Table 6.2: Vacancy formation energies (in eV) in bcc iron as calculated by EAM using Dudarev & Derlet’s<sup>8</sup> Case I and Case II, as well as Mendelev’s non-magnetic potential.<sup>138</sup>  $U_{\text{un}}^{\text{vac}}$  is the unrelaxed vacancy formation energy and  $U_{\text{f}}^{\text{vac}}$  is the relaxed value.

behaviour qualitatively although the magnitudes of the displacements are larger. Applying the damping factors has almost no effect on the BOP displacements. The results of the same calculations for the EAM potentials are shown in Fig. 6.3. Again, the first nearest neighbour relaxes strongly into the vacancy space while the relaxations of further shells are smaller and oscillating in sign.

The variation in magnetic moments around the unrelaxed vacancy is plotted as a function of the nearest neighbour shells in Fig. 6.4. As observed by Liu *et al.*,<sup>114</sup> the constraint of local charge neutrality within TB damps down the oscillations in magnetic moments surrounding the vacancy as compared to the case with no constraint on the charges. The DFT calculations, however, show an intermediate behaviour of the magnetic moments – they oscillate in sign but only by small amounts. The DFT calculation is also found to result in small amounts of charge transfer between atoms. Projecting onto spheres surrounding each atom with Wigner-Seitz radii of 1.45 Å (for PAW calculations, this value is determined automatically by VASP and corresponds to a ‘volume’ of 12.77 Å<sup>3</sup> per atom), the nearest-neighbour shell is found to lose 0.1 electrons per atom which are distributed amongst the other ‘bulk’ atoms. The absolute amount of charge transfer varies with an enforced Wigner-Seitz radius but the profile as a function of distance from the vacancy remains constant. The difference between TB and DFT may be due to the neglect of *s* electrons and *s-d* hybridisation in TB, the lack of a unique projection method to determine the local charges and magnetic moments in DFT, or the need for a more complex charge interaction in TB to account for these potentially small amounts of

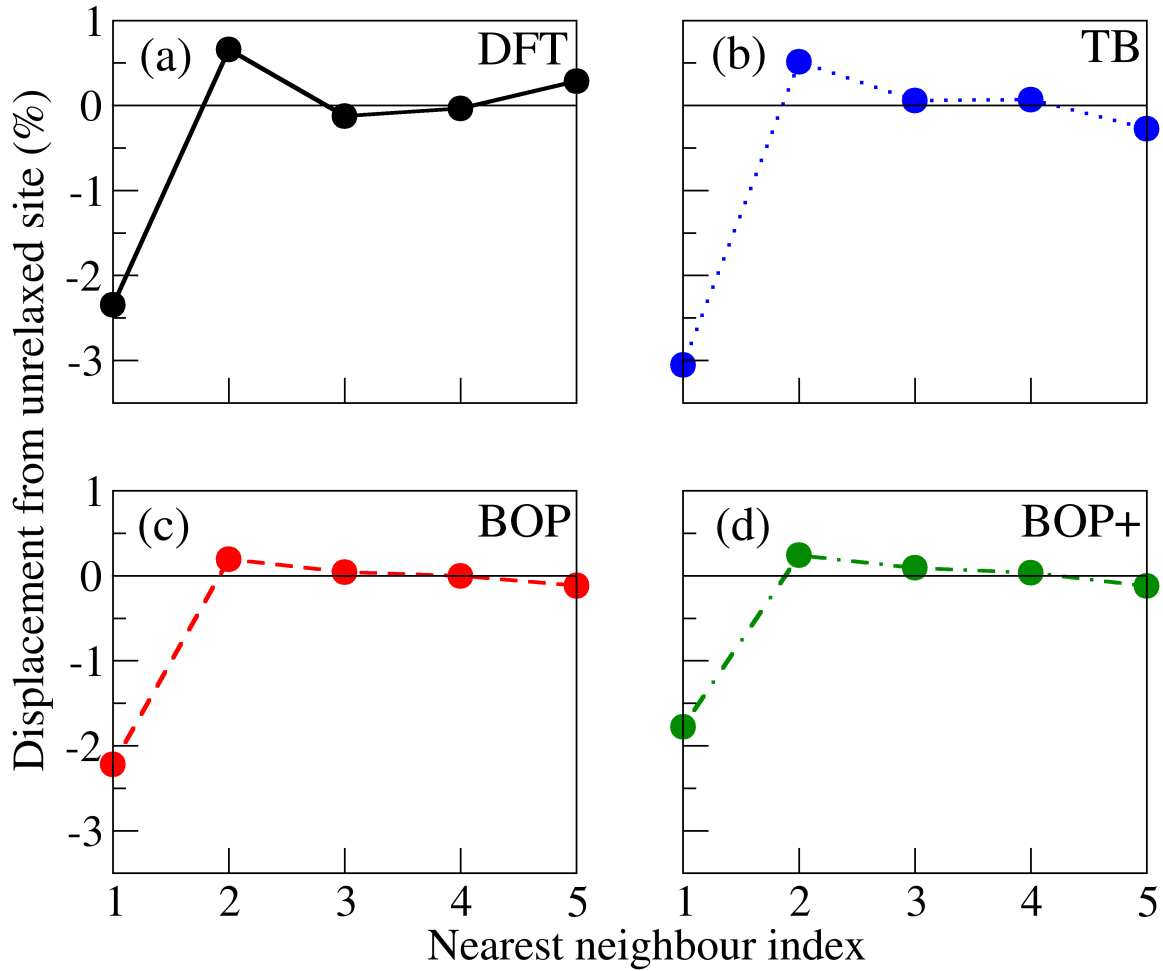


Figure 6.2: Nearest-neighbour shell relaxations about a vacancy at the centre of a 53 atom ferromagnetic bcc unit cell as calculated using (a) DFT, (b) TB, (c) 9-moment BOP and (d) 9-moment BOP+. Displacements are given relative to the position of the vacancy as a percentage of the initial unrelaxed distance.

interatomic charge transfer within the DFT calculation. Soin *et al.*<sup>115</sup> have introduced a finite Hubbard  $U$  term, equivalent to an onsite  $J_i$  in BOP, into their magnetic TB model for iron as an attempt to control charge transfer around a vacancy, but concluded that varying the value of  $U$  did not improve the agreement of the vacancy formation energy with DFT.

The behaviour of the magnetic moments both with and without LCN is qualitatively the same for 9-moment BOP. Calculations with unconstrained charges lead to strongly oscillating magnetic moments while the enforcement of an LCN state (by increasing the

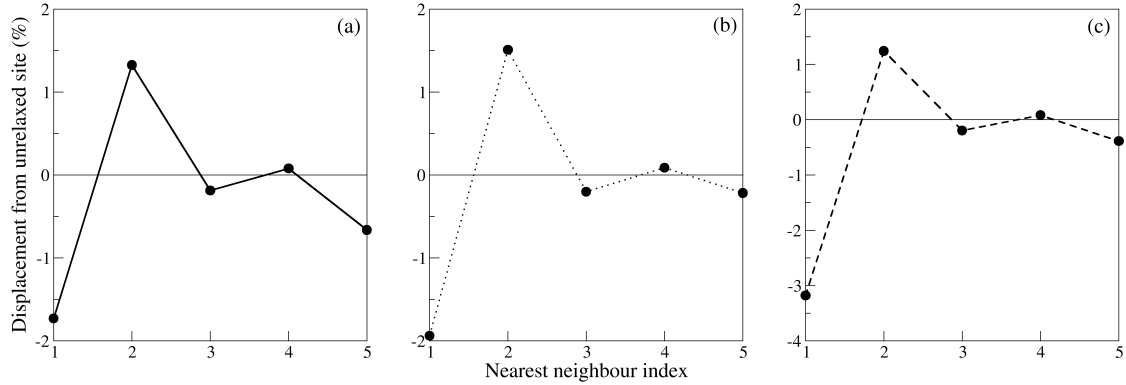


Figure 6.3: Nearest-neighbour shell relaxations about a vacancy at the centre of a 53 atom bcc unit cell as calculated with the EAM using (a) D & D Case I,<sup>8</sup> (b) D & D Case II<sup>8</sup> and (c) Mendelev's potential.<sup>138</sup> Displacements are given relative to the position of the vacancy as a percentage of the initial unrelaxed distance.

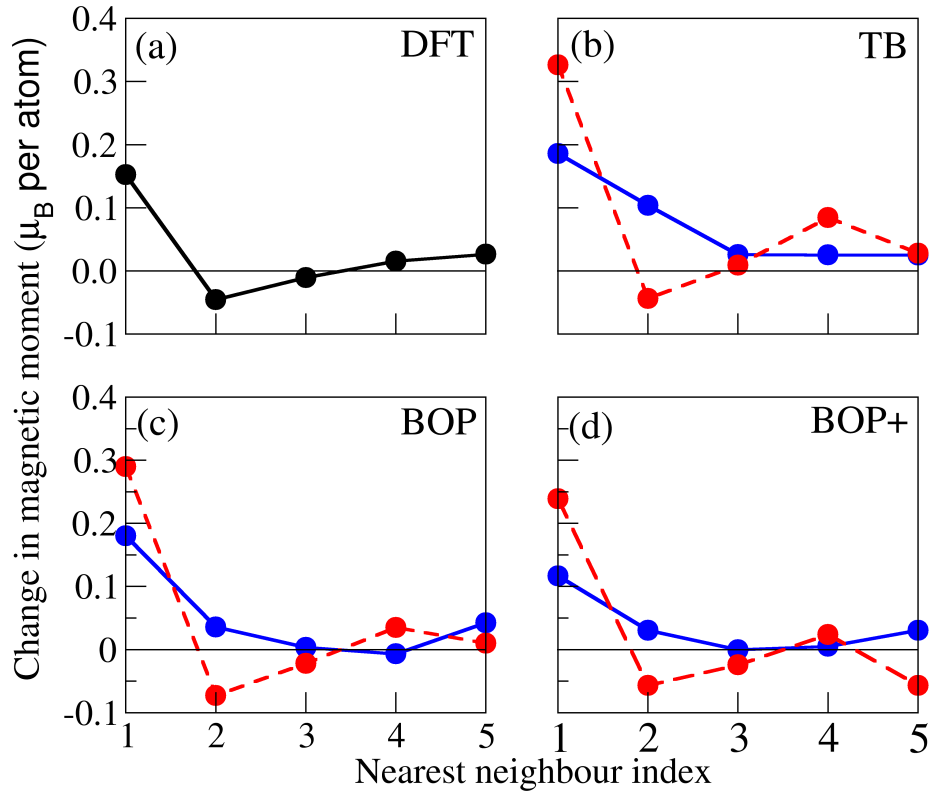


Figure 6.4: Local magnetic moments on neighbouring atoms about an unrelaxed vacancy at the centre of a 53 atom ferromagnetic bcc unit cell as calculated using (a) DFT, (b) TB, (b) 9-moment BOP and (d) 9-moment BOP+. Calculations with LCN ( $J_i = 15\text{eV}$ ) are marked solid blue, those with no charge constraints are dashed red.

$J_i$  contribution to 15 eV) damps the oscillations. Different behaviour is seen at the fifth nearest neighbour shell which may be a result of finite-size effects since these atoms lie at the boundary between neighbouring simulation cells. Applying the damping factors does not change the qualitative behaviour of the magnetic moments until the fifth neighbour.

The activation barrier to vacancy migration between two nearest-neighbour sites may be estimated by calculating the energy at the midpoint where the vacancy space is evenly distributed between the two sites, equivalent to moving a neighbouring atom to the point half-way between the sites. Table 6.3 shows this migration energy as calculated by DFT, TB and BOP, as well as EAM methods.

| Method | $U_{\text{mig}}$ | Method        | $U_{\text{mig}}$ |
|--------|------------------|---------------|------------------|
| DFT    | 0.64             | D & D Case I  | 0.96             |
| TB     | 0.70             | D & D Case II | 0.83             |
| BOP    | 0.85             | Mendelev      | 0.52             |
| BOP+   | 0.96             |               |                  |

Table 6.3: Table on left shows relaxed vacancy migration energies (in eV) in ferromagnetic bcc iron as calculated by PAW DFT, TB, 9-moment BOP and 9-moment BOP+. Table on right shows relaxed vacancy energies as calculated by three EAM potentials.

The experimental values for the vacancy migration energy vary between 0.5 eV and 1.3 eV depending on the method of measurement.<sup>158</sup> The DFT and TB values lie within the range of experimental data. Both BOP methods also lead to reasonable values of the migration energy.

### 6.2.2 Divacancy

The simplest multi-site defect is the divacancy. Previous studies have shown that the second vacancy in iron prefers to sit on a second nearest neighbour, rather than first nearest neighbour, lattice site. The calculated DFT, TB and BOP divacancy formation energies are given in Table 6.4.

As expected, the formation energy of the second nearest neighbour vacancy is lower than the first nearest neighbour in DFT. The energetic separation between the two structures is the same in TB, although the overall scale is reduced. This energy difference of 0.05 eV is too small to be resolved accurately by 9-moment BOP, both with and without the KPM damping factors.

The formation energy of two neighbouring vacancies is lower than two at infinite separation. The binding energies of the second nearest neighbour divacancies is also given in Table 6.4. The DFT vacancy binding energy agrees with published values,<sup>159</sup> which vary depending on the XC potential and DFT method used. The TB value is also in line with the published *ab initio* data and is reproduced well by BOP with the KPM damping factors.

| Method | $U_{\text{di}}^{1\text{NN}}$ | $U_{\text{di}}^{2\text{NN}}$ | Method | $U_B$ |
|--------|------------------------------|------------------------------|--------|-------|
| DFT    | 4.16                         | 4.11                         | DFT    | 0.18  |
| TB     | 3.49                         | 3.44                         | TB     | 0.28  |
| BOP    | 3.72                         | 3.84                         | BOP    | 0.18  |
| BOP+   | 3.81                         | 3.79                         | BOP+   | 0.25  |

Table 6.4: Table on left shows relaxed divacancy formation energies (in eV) in ferromagnetic bcc iron as calculated by PAW DFT, TB, 9-moment BOP and 9-moment BOP+.  $U_{\text{di}}^{1\text{NN}}$  is calculated for vacancies on first nearest neighbour sites,  $U_{\text{di}}^{2\text{NN}}$  for second nearest neighbours. Table on right show divacancy binding energies (in eV) for lowest energy configurations in ferromagnetic bcc iron as calculated by all four methods.

For comparison, both EAM models by Dudarev & Derlet<sup>8</sup> find almost exactly the same energy for the two configurations, slightly favouring the first nearest neighbour site. The Mendelev EAM model, on the other hand, finds the second nearest neighbour site to be 0.14 eV lower in energy (see Table 6.5). The divacancy binding energy for Case I is very low – the vacancy energy is almost completely site-independent – but those for Case II (which is fitted specifically to defect data) and the Mendelev potential agree with the published values.

| Method        | $U_{\text{di}}^{\text{1NN}}$ | $U_{\text{di}}^{\text{2NN}}$ | Method        | $U_B$ |
|---------------|------------------------------|------------------------------|---------------|-------|
| D & D Case I  | 4.08                         | 4.10                         | D & D Case I  | 0.06  |
| D & D Case II | 3.72                         | 3.73                         | D & D Case II | 0.24  |
| Mendelev      | 3.38                         | 3.24                         | Mendelev      | 0.20  |

Table 6.5: Table on left shows relaxed divacancy formation energies (in eV) in ferromagnetic bcc iron as calculated by three different EAM models.  $U_{\text{di}}^{\text{1NN}}$  is calculated for vacancies on first nearest neighbour sites,  $U_{\text{di}}^{\text{2NN}}$  for second nearest neighbours. Table on right shows divacancy binding energies (in eV) for lowest energy configurations in iron as calculated by all three models.

### 6.2.3 Self-interstitial atoms

The self-interstitial atom (SIA) defects are also important tests for a potential. These defects, however, present particular difficulties for simplified electronic structure methods because of the close proximity of the defect atoms. The SIA defect may be constructed by replacing one atom by two atoms in a large iron supercell, and then separating them symmetrically in space such that they resemble dumbbells lying along the  $\langle 100 \rangle$ ,  $\langle 110 \rangle$  or  $\langle 111 \rangle$  sets of crystallographic directions. Previous DFT and TB studies have found that the  $\langle 110 \rangle$  configuration is the lowest-energy interstitial defect in iron,<sup>160</sup> in agreement with X-ray scattering results.<sup>27</sup> This contrasts with the case of the non-magnetic bcc metals, where the preferred orientation is  $\langle 111 \rangle$ . The  $\langle 110 \rangle$  SIA is stabilised by the anti-ferromagnetic alignement of the local magnetic moments with respect to the bulk, and this configuration has a lower mobility than the  $\langle 111 \rangle$ , accounting for the increased threshold temperature for thermally-activated migration in iron.<sup>28</sup>

Complications which arose in the BOP relaxations led to the discovery of an anomaly in the TB electronic structure. In the unrelaxed SIA structures, sharp peaks appear several electronvolts above and below the main  $d$  band of the TB local DOS projected onto the interstitial atoms and their nearest neighbours (see Figure 6.5). Since the analytic BOP is derived to approximate simply connected bands, the sharp peaks and bandgaps in the TB DOS induce large oscillations throughout the BOP DOS and can lead to unphysical negative regions at the centre of the band. This means that not only are the BOP forces

inaccurate, but often convergence to a magnetic ground state also cannot be achieved. The bands corresponding to the spurious TB peaks are flat in  $k$ -space, implying that they are indeed localised on the interstitial atoms. Private communications with collaborators at ICAMS have confirmed that similar spurious peaks are found in TB calculations of carbon atoms in interstitial sites in iron. Additional peaks are also found in calculations with the Liu *et al.* TB model.<sup>114</sup> In this case (Fig. 6.6), the peaks are smaller in height but are still separated from the top of the main  $d$  band.

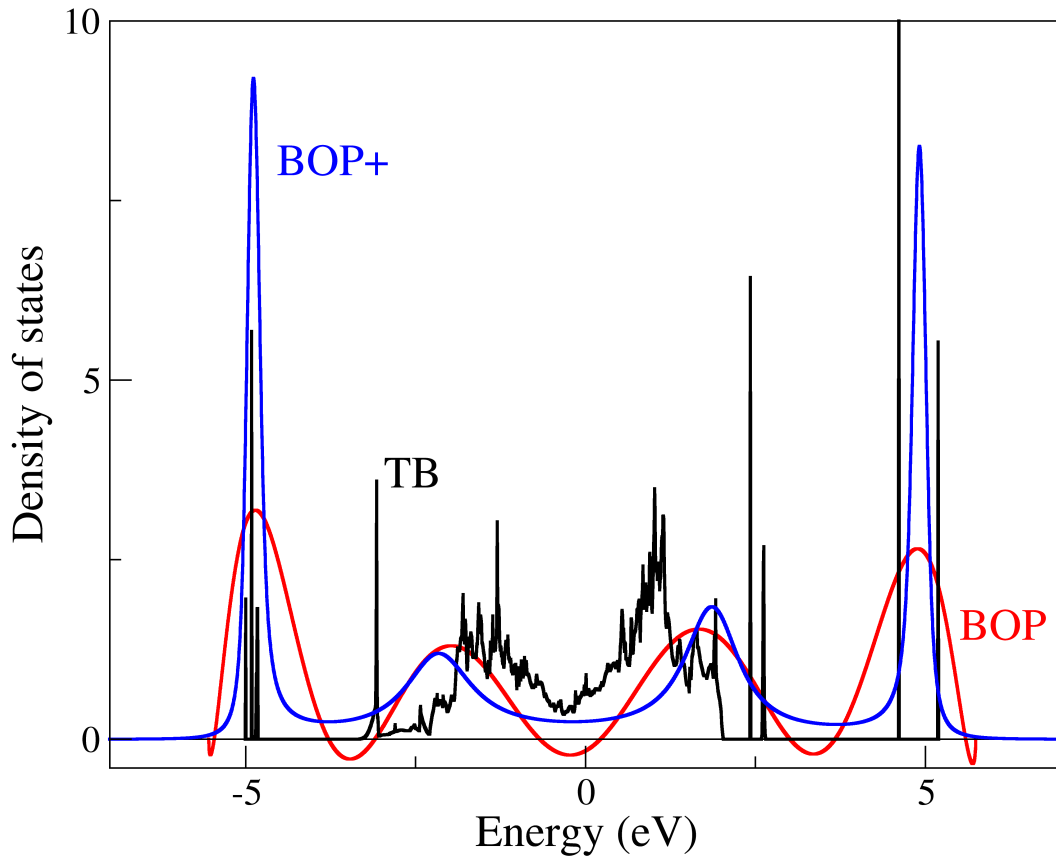


Figure 6.5: Local DOS on an unrelaxed  $\langle 110 \rangle$  self-interstitial atom calculated using the TB (black), 9-moment BOP (red) and 9-moment BOP+ (blue). This particular structure generates regions of negative density throughout the BOP DOS.

Localised states and band gaps had not been expected in calculations for  $d$ -only metals,

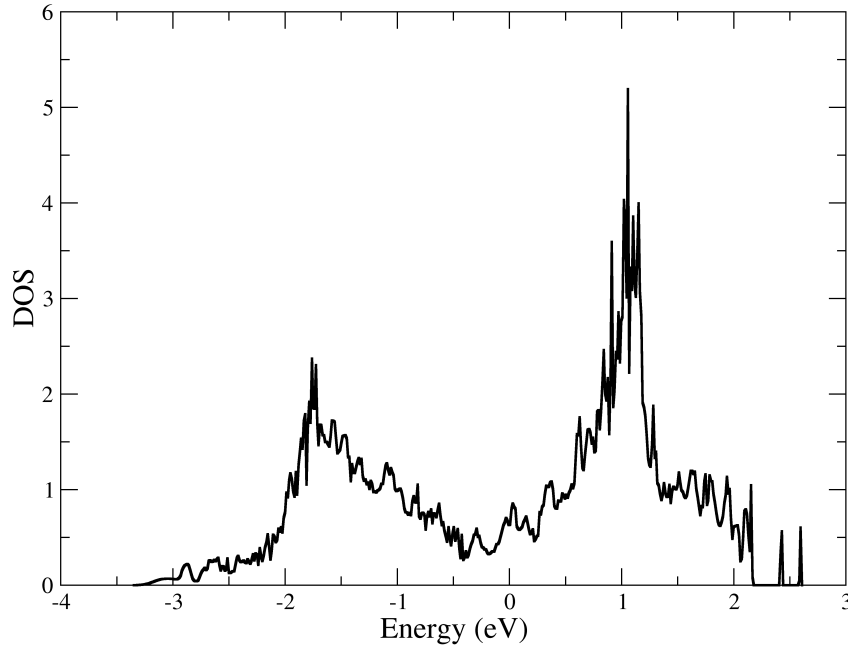


Figure 6.6: Local DOS on a relaxed  $\langle 110 \rangle$  self-interstitial atom calculated using the TB model of Liu *et al.*<sup>114</sup>

and these SIA calculations spurred the development of the BOP+ method. Figure 6.5 shows how the 9-moment BOP+ completely removes the negative regions of DOS seen with standard BOP, although at this level the detail of the main  $d$ -band is completely swamped by the much stronger peaks above and below.

Relaxation of the SIA defects was also problematic with TB because of the large initial forces on the atoms (over  $400 \text{ eV } \text{\AA}^{-1}$  for the unrelaxed structures). In order to reduce the forces on a starting TB configuration as far as possible, the structures were first relaxed using the EAM Case II potential of Dudarev & Derlet.<sup>8</sup> The EAM force calculation is extremely fast and allows for the use of a very small step size in the relaxation procedure to ensure that the relaxation is stable. Once the forces were reduced to below  $0.1 \text{ eV } \text{\AA}^{-1}$ , the structure could be relaxed more reliably with TB or BOP methods.

Once the TB structure is relaxed, the additional peaks move closer to the main band

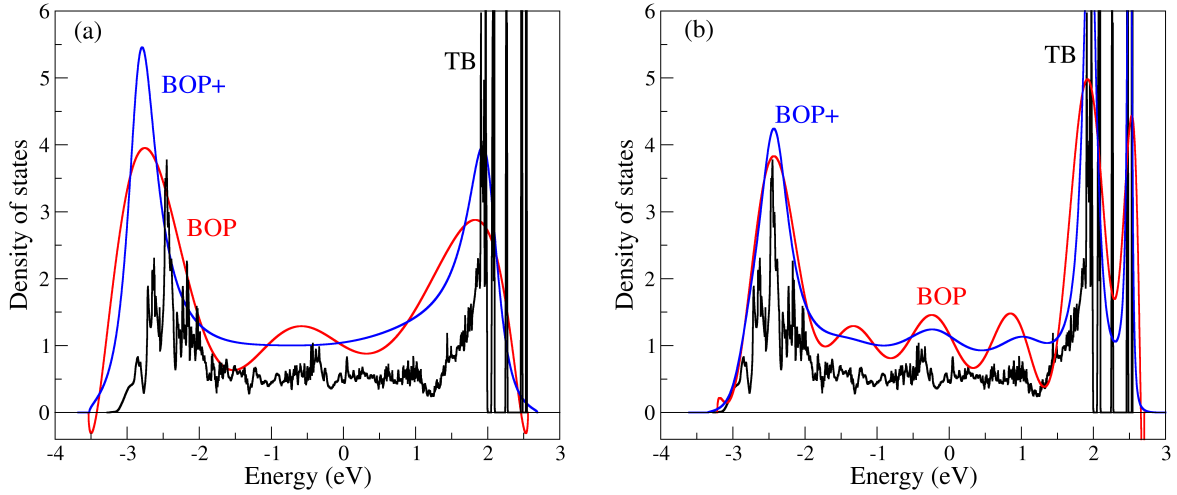


Figure 6.7: Local DOS on relaxed  $\langle 110 \rangle$  self-interstitial atom calculated using TB (black), BOP (red) and BOP+ (blue). BOP and BOP+ calculations used (a) 9 moments and (b) 15 moments.

(although they do not disappear) such that the analytic BOP method can be applied. Figure 6.7 shows the non-magnetic local DOS on an interstitial atom in the  $\langle 110 \rangle$  structure which has been relaxed fully in the magnetic state with TB. The non-magnetic densities of states calculated using BOP and BOP+ with (a) 9 moments and (b) 15 moments are superimposed. The band gaps between the extra peaks in the TB DOS are small enough that they do not cause negative regions to open up in the main BOP DOS. The general shape of the band, however, is less well reproduced than for the bulk and becomes more oscillatory as the number of exact moments is increased, caused by the strong peaks at the band edge. The oscillations obscure the detailed structure of the DOS in the centre of the band. Applying the KPM damping factors was found to lead to a much smoother convergence of the energy and the relaxation, and so those results are presented here.

The formation energies and local defect magnetic moments are presented in Table 6.6 and 6.7. While the TB model predicts the correct lowest energy configuration,  $\langle 110 \rangle$ , the formation energy of the defect is significantly underestimated compared to DFT.<sup>151,160</sup> Furthermore, the self-consistent calculations always lead to antiferromagnetic alignment

|           | $\langle 100 \rangle$ | $\langle 110 \rangle$ | $\langle 111 \rangle$ |
|-----------|-----------------------|-----------------------|-----------------------|
| TB        | 2.67                  | 2.16                  | 2.25                  |
| BOP+ (9)  | 1.61                  | 1.14                  | 1.49                  |
| BOP+ (12) | 2.45                  | 2.10                  | 2.37                  |
| DFT       | 4.64                  | 3.64                  | 4.34                  |

Table 6.6: Defect formation energies (eV) for interstitial atoms as calculated by 9- and 12-moment BOP+, TB, and DFT.

of the local moments for all three structures, whereas DFT finds only the  $\langle 110 \rangle$  SIA to be antiferromagnetic. The 9-moment BOP+ results show the same relative energetic ordering of the defects, but the scale is reduced even further. Moreover, while the  $\langle 100 \rangle$  and  $\langle 110 \rangle$  SIAs are found to be antiferromagnetic, the  $\langle 111 \rangle$  defect finds a lower energy with ferromagnetic alignment. All three defects are antiferromagnetic with 12-moment BOP+, but the increased formation energies are actually due to a further reduction in the local magnetic moments, rather than a convergence towards the TB result. This is perhaps not surprising given the large inaccuracies in the shape of the BOP DOS.

|           | $\langle 100 \rangle$ | $\langle 110 \rangle$ | $\langle 111 \rangle$ |
|-----------|-----------------------|-----------------------|-----------------------|
| TB        | -1.41                 | -1.60                 | -1.81                 |
| BOP+ (9)  | -0.64                 | -1.22                 | 1.37                  |
| BOP+ (12) | -0.24                 | -0.18                 | -0.79                 |

Table 6.7: Magnetic moments ( $\mu_B$ ) for interstitial atoms as calculated by 9- and 12-moment BOP and TB models.

While it is clear that this TB model does not provide a good description for the SIA defects, it is not obvious why the 9- or 12-moment BOP+ fails to find the same local magnetic states or the correct formation energies. Indeed, since the equilibrium atomic volume per atom is larger in the BOP+ structure, one might expect the BOP+ magnetic moments also to be larger than in TB. Starting the BOP+ calculations from the self-consistent TB onsite levels, relatively large charges are seen initially before the energy is subsequently minimised with respect to the onsite levels. This implies that the BOP+ charges are not converged particularly well, and an accurate BOP model would require

an adjusted value of  $N_d$ , if not a full reparametrisation. We return to this topic in section 7.5.3.

### 6.3 The (100) surface

The (100) surface is chosen as a simple test of extended defects because it has been studied previously by both experimental and theoretical methods. Furthermore, while the energetic ordering of the various possible surface terminations ((100), (110) and (111) being the most common) is found to be highly temperature-dependent in experiment, (100) is the most frequently observed cleavage plane in iron.<sup>161</sup> The structure of the (100) surface is the most open of the possible facets and so presents a particular challenge to the transferability of theoretical methods fitted for the bulk.

The surface is studied by simulating a slab of iron 16 atomic layers thick along the z-axis of a supercell. Periodic boundary conditions are applied in all three directions, with a spacing equivalent to 8 atomic layers included in the z-direction to prevent interactions between periodic images of the surface. For the TB and DFT calculations, a mesh of  $14 \times 14 \times 3$  k-points is used along the x-, y- and z-directions.

The energies of the relaxed (100) surface,  $\gamma_{(100)}$ , as calculated by DFT, TB, BOP and BOP+ are shown in Table 6.8. The surface energy is defined by

$$\gamma_{(100)} = \frac{N_{(100)}}{2A} (U_{(100)} - U_{\text{Bulk}}), \quad (6.2)$$

where  $N_{(100)}$  and  $U_{(100)}$  are the numbers of atoms and the energy per atom in the supercell containing the surface,  $U_{\text{Bulk}}$  is the energy per atom in the bulk and  $2A$  is the total surface area in the calculation. The surface energies as determined by all four methods are similar and compare favourably to previous DFT calculations ( $2.29 \text{ Jm}^{-2}$  and  $2.18 \text{ Jm}^{-2}$ )<sup>162, 163</sup> and experiment ( $2.41 \text{ Jm}^{-2}$ ).<sup>164</sup>

It is known that, in general, metallic surfaces tend to show an inwards contraction on

|      | $\gamma_{(100)}$ |
|------|------------------|
| DFT  | 2.51             |
| TB   | 2.30             |
| BOP  | 2.29             |
| BOP+ | 2.22             |

Table 6.8: (100) surface energies in  $\text{Jm}^{-2}$  as calculated with DFT, TB, 9-moment BOP, and 9-moment BOP+. A slab 16 atoms thick is used in the supercell calculation.

relaxation. Previous theoretical calculations have shown that while the first layer in the (100) surface contracts, the second and third layers expand.<sup>162</sup> In the transition metals, this surface contraction can be explained by a spilling-out of the delocalised *sp* electrons into the surrounding vacuum, allowing the more tightly-bound *d* bonds to exert an inwards force on the outermost layer.<sup>165</sup> The oscillatory nature of the expansions and contractions is a result of this competition between the *sp* and *d* electronic forces acting on the atoms. The changes in the first surface layer interplanar spacing,  $\delta d_{12}$ , as a percentage of the bulk interplanar spacing are compared in Table 6.9. A negative value of  $\delta d_{12}$  translates to a contraction of the surface while a positive value means an expansion.

|      | $\delta d_{12}^{\text{FM}}$ | $\delta d_{12}^{\text{NM}}$ |
|------|-----------------------------|-----------------------------|
| DFT  | -1.73%                      | -13.93%                     |
| TB   | 2.41%                       | -22.56%                     |
| BOP  | 1.67%                       | -26.28%                     |
| BOP+ | 3.20%                       | -25.62%                     |

Table 6.9: The change in first interplanar spacing,  $\delta d_{12}$ , for ferromagnetic and non-magnetic (100) bcc surfaces given as a percentage of the bulk interplanar spacing.

Density functional calculations agree with the literature that the (100) surface of ferromagnetic bcc contracts on relaxation. The TB and BOP calculations, however, show the surface expanding into the vacuum. It appears that this expansion is driven by an unphysically large increase in the local magnetic moments at the surface (see Fig. 6.8). In general, the enhancement of magnetic polarisation at the surface can be explained by a narrowing of the local *d* band due to the reduced atomic coordination. The particular

TB (and hence BOP) model is known to overestimate the bulk magnetic moment and this leads to almost complete magnetic saturation at the surface. The large surface moments lower the exchange energy further, leading to a magnetic pressure driving the surface to expand. In fact, repeating the calculations with the same geometry, but with spin polarisation turned off, leads to a very strong contraction of the surface with all methods (see Table 6.9). The magnetic expansive force which balances the non-magnetic tendency towards strong contraction is therefore overestimated by the TB parametrisation. The very strong non-magnetic contraction compared to DFT may be due to the neglect of the *sp* electrons which counteract the *d* forces on the atoms. In this case, we find that the ultimate accuracy of the BOP calculations is controlled by the underlying TB model.

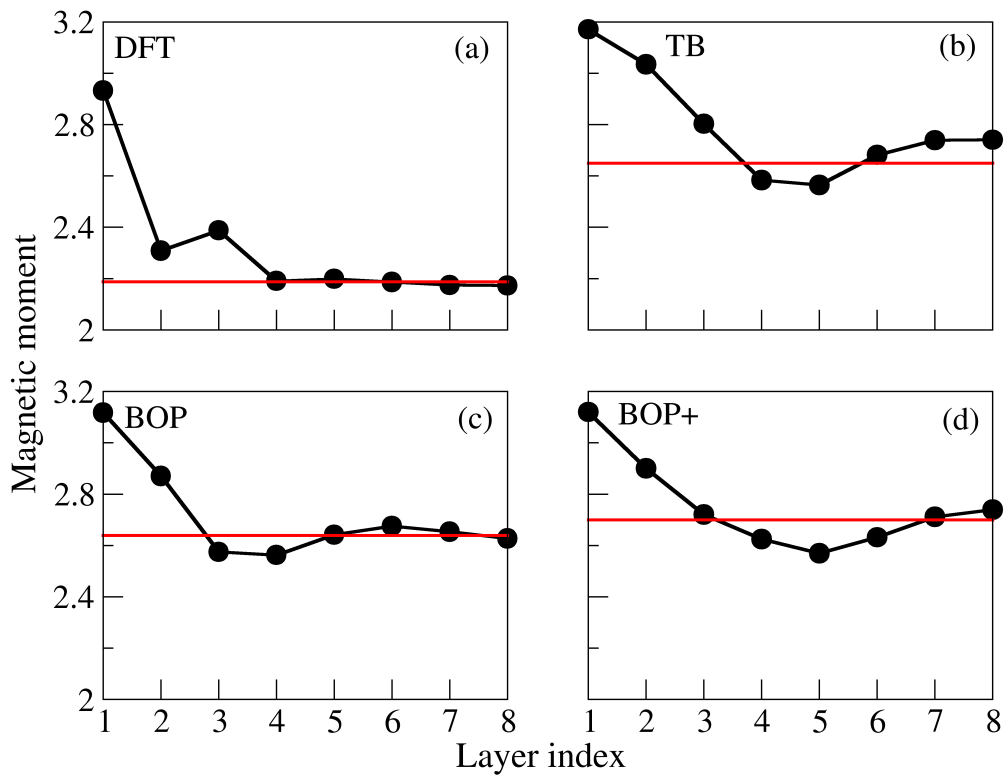


Figure 6.8: Magnetic moments (black) as a function of distance from the bcc (100) surface relative to the bulk value (red) as calculated by (a) DFT, (b) TB, (c) 9-moment BOP and (d) 9-moment BOP with the Jackson kernel.

The qualitatively different behaviours between DFT and TB/BOP may also be influenced by local charge transfer. The self-consistent spin-polarised DFT calculations show

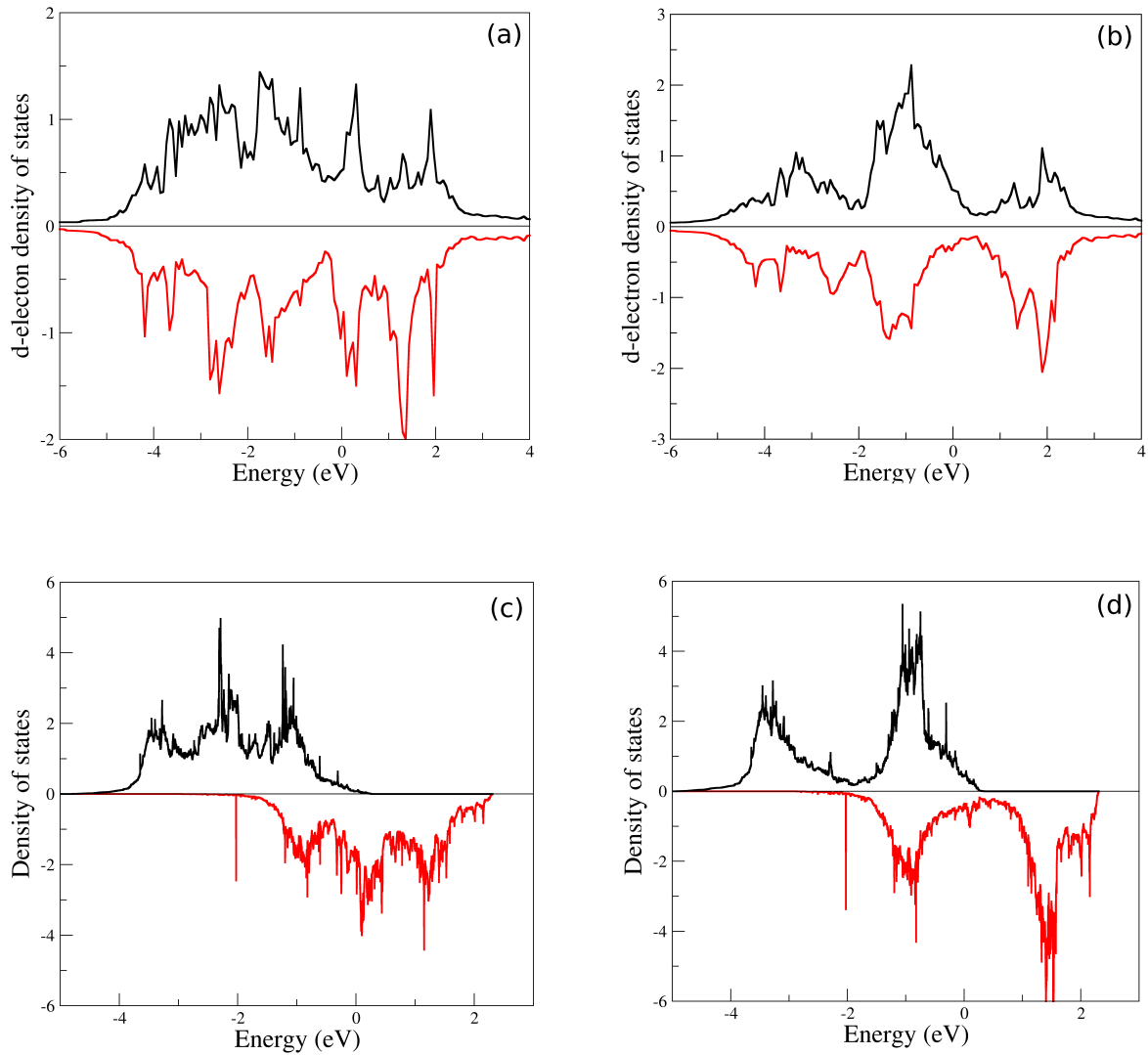


Figure 6.9: *d*-projected DFT local DOS plotted for (a) first and (b) second atomic layers from the (100) surface of FM bcc iron. Equivalent TB local DOS are shown in (c) for the first and (d) for the second atomic layers

the surface atoms to lose 0.36 electrons each which are spread evenly amongst the atoms forming the ‘bulk’ of the slab. Previous calculations also found a transfer of around 0.5 electrons from the surface atoms to the subsurface layers.<sup>163</sup> This charge transfer not only introduces a Coulombic energy term but also modifies the stable magnetic moments and hence the magnetic energy. This effect is neglected in locally charge-neutral TB and BOP calculations.

The (100) surface is a case where achieving convergence with the BOP becomes prob-

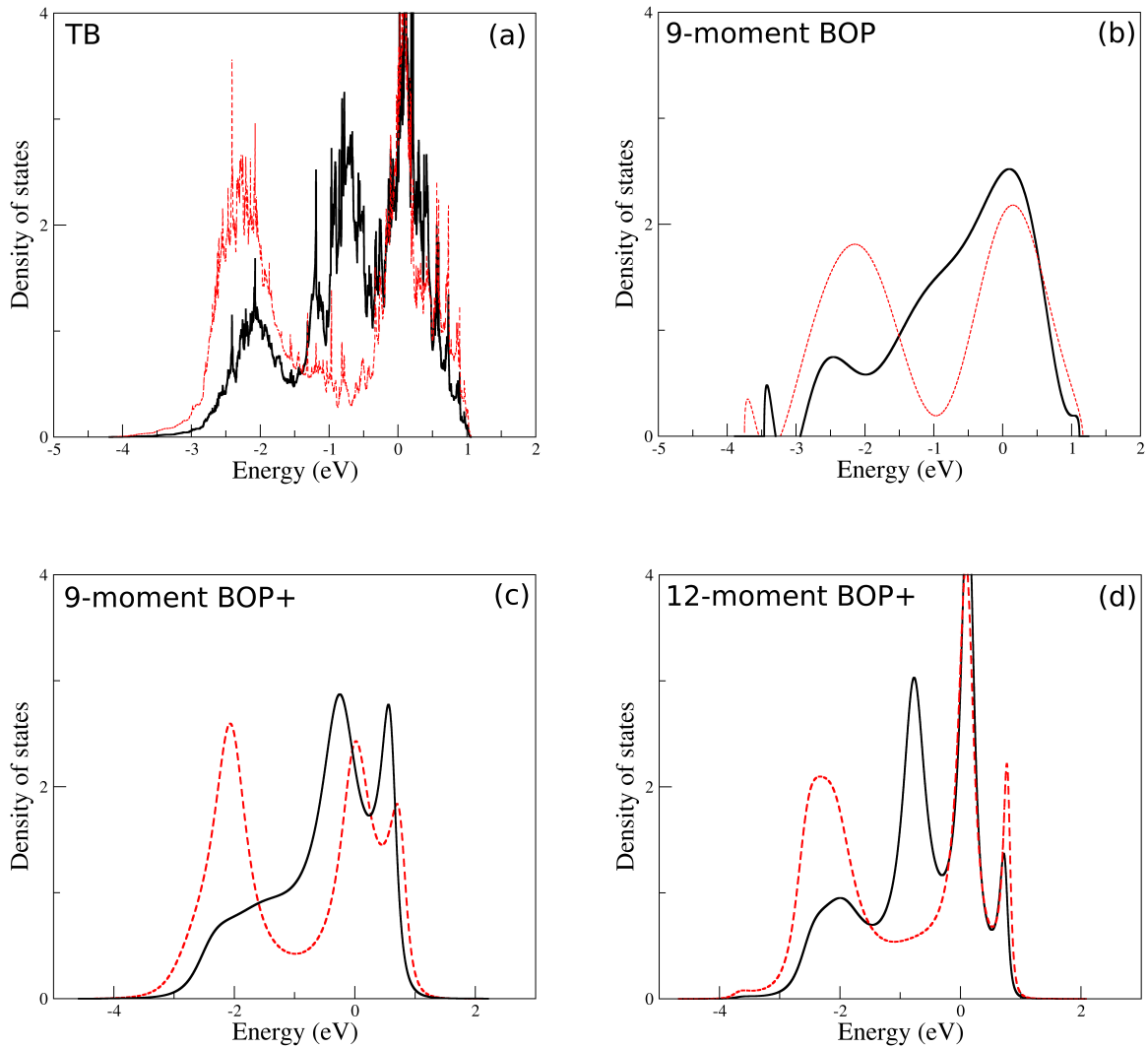


Figure 6.10: Non-magnetic local DOS plotted for first (black) and second (red) atomic layers from the (100) surface of bcc iron. TB calculations are shown in (a), 9-moment BOP in (b), 9-moment BOP+ in (c) and 12-moment BOP+ in (d).

lematic because of negative densities of states. The local DOS is significantly modified at the surface, as seen in the site-projected DFT data (see Fig. 6.9). The  $d$  band DOS shows a third peak in the centre of the band, closing the bulk bcc pseudogap. The DOS shape has returned to the general bulk structure by the second atomic layer. The TB model is able to reproduce this behaviour (Fig. 6.9). Low-moment BOP expansions, however, are not able to resolve the surface peak (Fig. 6.10). In fact, during self-consistent calculations the local DOS often becomes negative in the centre of the band and so the calculation

diverges. The BOP calculations had to be performed starting from the self-consistent TB onsite levels so that a realistic solution could be achieved. Applying the Jackson kernel damping factors removes the possibility of negative DOS and the calculations converge much more smoothly to a solution. The surface peak is still not reproduced well by low-moment expansions, although it is clearly visible once 12 exact moments have been included (Fig. 6.10).

## 6.4 Summary

The analytic BOP method (both with and without the Jackson kernel) has been compared to exact TB results using the model by Madsen *et al.*<sup>101</sup> Simple defects such as the monovacancy and divacancy are described well by the 9-moment BOP model, but the self-interstitial atoms prove a greater challenge for the method. Localised states have been detected on interstitial atoms, leading to sharp peaks in the local DOS and small bandgaps. The analytic BOP method is derived for the case of a connected band and is not able to reproduce the SIA DOS accurately. The incorrect magnetic states found on the defects as compared to DFT results are, however, also present in the TB calculations. Furthermore, the particular TB parametrisation also leads to an expansion of the (100) surface on relaxation, as opposed to the *ab initio* and experimentally observed contraction. This expansion appears to be driven by an overestimation of the surface magnetic moments and could be a restriction of a  $d$  only model, which is replicated by the BOP.

# Chapter 7

## Non-collinear magnetism in analytic BOP

### 7.1 Introduction

Drautz & Pettifor have shown<sup>17</sup> how magnetism may be described within the formalism of the analytic BOP method in a general sense, for both collinear and non-collinear magnetic configurations. While in the collinear case the global  $\uparrow\uparrow$  and  $\downarrow\downarrow$  spin channels decouple, leading to a simple extension of the non-magnetic BOP method to two separate spin bands per atom, this no longer holds when the spins on adjacent atoms are canted. In this case, the interference (and transfer) paths must be calculated in the global spin-space, while the BOP expansion is performed in a locally-rotated spin-space on each atom. Although the modifications required for the calculation of the charges, magnetic moments and energy are relatively simple, the expressions for the gradients are more involved. The discussion of the practical calculation of the gradients will be more in-depth than in Ref. [17] and some novel expressions are derived. Some simple results for non-collinear configurations in iron will be demonstrated.

## 7.2 Background theory

### 7.2.1 Rotations in spin-space

For non-collinear magnetic configurations, a *global* axis for spin quantisation may no longer be defined, which instead varies locally from site to site in the crystal. In this case two related coordinate systems are defined: the global coordinate system where interactions between different sites must be evaluated, and the local coordinate system on each atom where the  $z$  direction is rotated to point along the magnetic moment vector.

In general, a quantity defined by a  $2 \times 2$  matrix in the global spin-space,  $\Lambda^{(\text{gl})}$ ,

$$\Lambda^{(\text{gl})} = \begin{pmatrix} \Lambda_{(\text{gl})}^{\uparrow\uparrow} & \Lambda_{(\text{gl})}^{\uparrow\downarrow} \\ \Lambda_{(\text{gl})}^{\downarrow\uparrow} & \Lambda_{(\text{gl})}^{\downarrow\downarrow} \end{pmatrix}, \quad (7.1)$$

may be rotated into the local spin-space by the unitary transformation

$$\Lambda^{(\text{l})} = \mathbf{U} \Lambda^{(\text{gl})} \mathbf{U}^\dagger, \quad (7.2)$$

or in terms of matrix elements,

$$\Lambda_{\mu\nu}^{(\text{l})} = \sum_{\tau=1}^2 \sum_{\omega=1}^2 U_{\mu\tau} \Lambda_{\tau\omega}^{(\text{gl})} U_{\omega\nu}^\dagger. \quad (7.3)$$

The inverse transformation is given by

$$\Lambda^{(\text{l})} = \mathbf{U}^\dagger \Lambda^{(\text{gl})} \mathbf{U}. \quad (7.4)$$

The transformation matrix,  $\mathbf{U}$ , is defined by<sup>166</sup>

$$\mathbf{U} = \exp \left( -i \frac{\alpha}{2} \boldsymbol{\sigma} \cdot \mathbf{n} \right), \quad (7.5)$$

where  $\alpha$  is the angle between the  $z$  direction in the global space,  $\mathbf{s}^{(\text{gl})}$ , and the direction

of the local magnetic moment,  $\mathbf{s}_{i\alpha}^{(l)}$ ,

$$\cos(\alpha) = \mathbf{s}^{(gl)} \cdot \mathbf{s}_{i\alpha}^{(l)}. \quad (7.6)$$

The vector  $\mathbf{n}$ , orthogonal to both directions, is defined by

$$\mathbf{n} = \frac{\mathbf{s}^{(gl)} \times \mathbf{s}_{i\alpha}^{(l)}}{|\mathbf{s}^{(gl)} \times \mathbf{s}_{i\alpha}^{(l)}|}, \quad (7.7)$$

and  $\boldsymbol{\sigma}$  is the vector of Pauli matrices. The expression for  $\mathbf{U}$  is simplified, by taking a Taylor expansion, to

$$\mathbf{U} = \cos\left(\frac{\alpha}{2}\right) \mathbf{1} - i(\boldsymbol{\sigma} \cdot \mathbf{n}) \sin\left(\frac{\alpha}{2}\right), \quad (7.8)$$

where  $\mathbf{1}$  is the identity matrix. By definition of being a unitary matrix,  $\mathbf{U}$  satisfies the conditions

$$\mathbf{U}\mathbf{U}^\dagger = \mathbf{U}^\dagger\mathbf{U} = \mathbf{1}, \quad (7.9)$$

and

$$\mathbf{U}^\dagger = \mathbf{U}^{-1}, \quad (7.10)$$

where  $\mathbf{U}^{-1}$  is the inverse of  $\mathbf{U}$ .

### 7.2.2 Construction of the local DOS

The Hamiltonian for the non-collinear system may be defined as for the general magnetic TB case, Eqn. (3.39),

$$E_{i\alpha\mu\nu} = E_{i\alpha}^{(0)}\delta_{\mu\nu} + \mathbf{B}_i \cdot \boldsymbol{\sigma}_{\mu\nu} - \frac{1}{2}I_i\mathbf{m}_i \cdot \boldsymbol{\sigma}_{\mu\nu} + J_iq_i, \quad (7.11)$$

Shifts due to magnetism are taken only to apply to these onsite elements of the Hamiltonian. Furthermore, we define an onsite level matrix for each site which is  $2 \times 2$  in

spin-space,

$$\mathbf{E}_{i\alpha}^{(\text{gl})} = \begin{pmatrix} E_{i\alpha}^{\uparrow\uparrow} & E_{i\alpha}^{\uparrow\downarrow} \\ E_{i\alpha}^{\downarrow\uparrow} & E_{i\alpha}^{\downarrow\downarrow} \end{pmatrix}. \quad (7.12)$$

By construction of the onsite levels, Eqn. (7.11), this matrix is diagonalised by a rotation into the local coordinate frame,

$$\mathbf{E}_{i\alpha}^{(\text{l})} = \mathbf{U} \mathbf{E}_{i\alpha}^{(\text{gl})} \mathbf{U}^\dagger = \begin{pmatrix} E_{i\alpha}^\uparrow & 0 \\ 0 & E_{i\alpha}^\downarrow \end{pmatrix}. \quad (7.13)$$

Since in the general non-collinear case the rotation matrices are site-dependent, the moments of the local DOS must be calculated globally from the products of the Hamiltonian at each site,

$$\mu_{i\alpha\mu\nu}^{(p,\text{gl})} = \sum_{\substack{i_1\alpha_1\nu_1, \\ i_2\alpha_2\nu_2, \\ \dots, \\ i_{p-1}\alpha_{p-1}\nu_{p-1}}} H_{i\alpha\mu i_1\alpha_1\nu_1} H_{i_1\alpha_1\nu_1 i_2\alpha_2\nu_2} \cdots H_{i_{p-1}\alpha_{p-1}\nu_{p-1} i\alpha\nu}. \quad (7.14)$$

This means that all four quadrants of the Hamiltonian in the global spin-space are included, and this differs from the collinear case where the  $\uparrow\uparrow$  and  $\downarrow\downarrow$  quadrants can be treated separately. The resulting moments matrix is Hermitian and may have complex off-diagonal elements. The  $\mu_{i\alpha\mu\nu}^{(p,\text{gl})}$  may be rotated into the local coordinate system on each atom using the same rotation matrices as for Eqn. (7.13), although this transformation need not diagonalise the moments matrix in spin space (unless  $p = 1$ ),

$$\boldsymbol{\mu}_{i\alpha}^{(p,\text{l})} = \mathbf{U}_{i\alpha} \boldsymbol{\mu}_{i\alpha}^{(p,\text{gl})} \mathbf{U}_{i\alpha}^\dagger = \begin{pmatrix} \mu_{i\alpha\mu\uparrow\uparrow}^{(p,\text{l})} & \mu_{i\alpha\mu\uparrow\downarrow}^{(p,\text{l})} \\ \mu_{i\alpha\mu\downarrow\uparrow}^{(p,\text{l})} & \mu_{i\alpha\mu\downarrow\downarrow}^{(p,\text{l})} \end{pmatrix}. \quad (7.15)$$

This is because the global moments contain contributions coming from neighbouring sites with different local spin orientations.

However, defining  $\mu_{i\alpha\uparrow}^{(p)} = \mu_{i\alpha\uparrow\uparrow}^{(p,\text{l})}$  and  $\mu_{i\alpha\downarrow}^{(p)} = \mu_{i\alpha\downarrow\downarrow}^{(p,\text{l})}$ , which are both real, and neglecting

the complex off-diagonal elements of  $\boldsymbol{\mu}_{i\alpha}^{(p,l)}$ , we are once again able to separate the BOP expansion for the up- and down-spin DOS on each atom. This approximation makes the expressions for the charge, magnetic moment and energy, already defined for the collinear case, locally applicable.  $N_{i\alpha}^\uparrow - N_{i\alpha}^\downarrow$  then defines the magnitude of the output magnetic moment along  $\mathbf{s}_{i\alpha}^{(l)}$ . The damping factors of the KPM may also be applied just as for the collinear case.

## 7.3 Extensions to theory

### 7.3.1 Derivatives of the energy

As we have seen, the expressions for the local charges, magnetic moments and energy as defined for collinear magnetism are still valid if we consider only the diagonal elements of the moments matrix after rotation into the local coordinate space. The expansion of the derivatives, however, is more involved as the multiplication of factors on neighbouring sites must be performed in the global spin-space.

In the published theory, the expression for the total derivative of the energy is given by Eqn. (4.43),

$$\frac{dU_B}{d\Lambda} = \sum_{i\alpha\nu} \sum_{n=0}^{n_{\max}} w_{i\alpha\nu}^{(n)} \frac{d\mu_{i\alpha\nu}^{(n)}}{d\Lambda} - \sum_{i\alpha\nu} N_{i\alpha\nu} \frac{dE_{i\alpha\nu}}{d\Lambda} + \frac{dU_{\text{rep}}}{d\Lambda}. \quad (7.16)$$

However, the rearrangement of this equation to give a Hellmann-Feynman-like form, Eqn. (4.49),

$$\frac{dU_B}{dE_{i\alpha\nu}} = \tilde{\Theta}_{i\alpha\nu i\alpha\nu} - N_{i\alpha\nu}, \quad (7.17)$$

holds only when the rotation matrices on each site are identical; that is to say, it is only valid for collinear magnetism. We find instead that these equations must be modified

such that the moments and the weights become  $2 \times 2$  matrices in spin-space,

$$\frac{dU_B}{d\Lambda} = \sum_{i\alpha} \sum_{n=0}^{n_{\max}} \text{Tr} \left( \mathbf{w}_{i\alpha}^{(n,\text{gl})} \frac{d\boldsymbol{\mu}_{i\alpha}^{(n,\text{gl})}}{d\Lambda} \right) - \sum_{i\alpha\nu} N_{i\alpha\nu} \frac{dE_{i\alpha\nu}}{d\Lambda} + \frac{dU_{\text{rep}}}{d\Lambda}, \quad (7.18)$$

where

$$\frac{d\boldsymbol{\mu}_{i\alpha}^{(n,\text{gl})}}{d\Lambda} = \begin{pmatrix} \frac{d\mu_{i\alpha\uparrow\uparrow}^{(n,\text{gl})}}{d\Lambda} & \frac{d\mu_{i\alpha\uparrow\downarrow}^{(n,\text{gl})}}{d\Lambda} \\ \frac{d\mu_{i\alpha\downarrow\uparrow}^{(n,\text{gl})}}{d\Lambda} & \frac{d\mu_{i\alpha\downarrow\downarrow}^{(n,\text{gl})}}{d\Lambda} \end{pmatrix}. \quad (7.19)$$

Since in the local coordinate system we consider only the  $\uparrow$  and  $\downarrow$  DOS on each atom, the local weights are constructed from Eqn. (4.45),

$$w_{i\alpha\nu}^{(n,l)} = \frac{\partial U_{\text{band}}}{\partial \mu_{i\alpha\nu}^{(n)}} + \left( E_{i\alpha\nu} - \frac{\sum_{j\beta\mu} E_{j\beta\mu} n_{j\beta\mu}(E_F)}{\sum_{j\beta\mu} n_{j\beta\mu}(E_F)} - \frac{1}{2} \left( (-1)^\nu I_i m_i - \frac{\sum_{j\beta\mu} (-1)^\mu I_j m_j n_{j\beta\mu}(E_F)}{\sum_{j\beta\mu} n_{j\beta\mu}(E_F)} \right) \right) \frac{\partial}{\partial \mu_{i\alpha\nu}^{(n)}} \int^{E_F} n_{i\alpha\nu} dE, \quad (7.20)$$

such that they are diagonal in spin space,

$$\mathbf{w}_{i\alpha}^{(n,l)} = \begin{pmatrix} w_{i\alpha\uparrow}^{(n,l)} & 0 \\ 0 & w_{i\alpha\downarrow}^{(n,l)} \end{pmatrix}. \quad (7.21)$$

The global weights in Eqn. (7.18),  $\mathbf{w}_{i\alpha}^{(n,\text{gl})}$ , are generated from their local counterparts by the rotation

$$\mathbf{w}_{i\alpha}^{(n,\text{gl})} = \mathbf{U}_{i\alpha}^\dagger \mathbf{w}_{i\alpha}^{(n,l)} \mathbf{U}_{i\alpha}, \quad (7.22)$$

and now acquire two spin indices.

A global bond-order term,  $\tilde{\Theta}_{i\alpha\mu j\beta\nu}^{(\text{gl})}$ , may then be defined in matrix notation as

$$\tilde{\Theta}_{i\alpha j\beta}^{(\text{gl})} = \sum_{n=1}^{n_{\max}} \Xi_{i\alpha j\beta}^{(n-1,n)}, \quad (7.23)$$

where

$$\Xi_{i\alpha j\beta}^{(n-1,n)} = \mathbf{T}_{i\alpha j\beta}^{(n-1,m)} + \mathbf{w}_{i\alpha}^{(m,\text{gl})} \boldsymbol{\xi}_{i\alpha j\beta}^{(n-1)}. \quad (7.24)$$

The transfer paths are updated iteratively according to

$$\mathbf{T}_{i\alpha j\beta}^{(n,m)} = \sum_{k\gamma} \mathbf{H}_{i\alpha k\gamma} \left( \mathbf{T}_{k\gamma j\beta}^{(n-1,m)} + \mathbf{w}_{k\gamma}^{(m,\text{gl})} \boldsymbol{\xi}_{k\gamma j\beta}^{(n-1)} \right). \quad (7.25)$$

The correct order of the matrix multiplications is necessary to ensure that  $\tilde{\Theta}_{i\alpha\mu j\beta\nu}^{(\text{gl})}$  remains Hermitian (that is to say that  $\tilde{\Theta}_{i\alpha\mu j\beta\nu}^{(\text{gl})} = \tilde{\Theta}_{i\alpha\mu j\beta\nu}^{(\text{gl})\dagger}$ ). These additional rotations into the global space are missing from the original magnetic analytic BOP formulation. Therefore, the expressions in Section IV D of Ref. [17] were found to be incomplete for a practical implementation of the method.

The gradient of the binding energy with respect to the local up- and down-spin onsite levels is given by

$$\frac{\partial U_B}{\partial E_{i\alpha\nu}} = \tilde{\Theta}_{i\alpha\nu i\alpha\nu}^{(l)} - N_{i\alpha\nu}, \quad (7.26)$$

where

$$\tilde{\Theta}_{i\alpha j\beta}^{(l)} = \mathbf{U}_{i\alpha} \tilde{\Theta}_{i\alpha j\beta}^{(\text{gl})} \mathbf{U}_{i\alpha}^\dagger. \quad (7.27)$$

The energy may be minimised with respect to these two degrees of freedom per atom, equivalent to a minimisation with respect to the charge and the magnitude of the magnetic moment along  $\mathbf{s}_{i\alpha}^{(l)}$ . This corresponds to a constrained non-collinear minimisation in TB or DFT, except that the contributions from the off-diagonal elements of the density matrix are neglected (see section 4.49). The local onsite levels must be rotated back into the global Hamiltonian, according to Eqn. (7.4), for the evaluation of the new moments at each step in the energy minimisation process.

The expression for the force on atom  $k$  involves only the intersite elements of the bond-order and the Hamiltonian matrices, since it is only defined once the energy is already minimised with respect to the onsite levels,

$$\nabla_k U_B = \sum_{i\alpha \neq j\beta} \sum_{\nu} \tilde{\Theta}_{i\alpha\nu j\beta\nu}^{(l)} \nabla_k H_{j\beta\nu i\alpha\nu} + \nabla_k U_{\text{Rep}} = \sum_{i\alpha \neq j\beta} \tilde{\Theta}_{i\alpha\mu j\beta\nu}^{(\text{gl})} \nabla_k H_{j\beta\nu i\alpha\mu} + \nabla_k U_{\text{Rep}}. \quad (7.28)$$

This equality is valid since only the onsite elements of the Hamiltonian are affected by the rotation  $\mathbf{U}$ .

The torque is a vector quantity defined as the change in total energy on rotation of the local magnetic moment direction,  $\mathbf{s}_{i\alpha}^{(l)}$ . Both the moments of the DOS and the rotation matrices,  $\mathbf{U}_{i\alpha}$ , depend on  $\mathbf{s}_{i\alpha}^{(l)}$ . Therefore, the relation between the derivative of the local moments,  $\frac{d\boldsymbol{\mu}_{i\alpha}^{(n,l)}}{d\mathbf{s}_{i\alpha}^{(l)}}$ , and the global moments,  $\frac{d\boldsymbol{\mu}_{i\alpha}^{(n,gl)}}{d\mathbf{s}_{i\alpha}^{(l)}}$ , also contains derivatives of the rotation matrices themselves,

$$\frac{d\boldsymbol{\mu}_{i\alpha}^{(n,l)}}{d\mathbf{s}_{i\alpha}^{(l)}} = \frac{d\mathbf{U}_{i\alpha}}{d\mathbf{s}_{i\alpha}^{(l)}} \boldsymbol{\mu}_{i\alpha}^{(n,gl)} \mathbf{U}_{i\alpha}^\dagger + \mathbf{U}_{i\alpha} \frac{d\boldsymbol{\mu}_{i\alpha}^{(n,gl)}}{d\mathbf{s}_{i\alpha}^{(l)}} \mathbf{U}_{i\alpha}^\dagger + \mathbf{U}_{i\alpha} \boldsymbol{\mu}_{i\alpha}^{(n,gl)} \frac{d\mathbf{U}_{i\alpha}^\dagger}{d\mathbf{s}_{i\alpha}^{(l)}}. \quad (7.29)$$

The torque is defined by

$$\frac{dU_B}{d\mathbf{s}_{k\gamma}^{(l)}} = \sum_{i\alpha} \text{Tr} \left( \mathbf{w}_{i\alpha}^{(n,l)} \frac{d\boldsymbol{\mu}_{i\alpha}^{(n,l)}}{d\mathbf{s}_{k\gamma}^{(l)}} \right), \quad (7.30)$$

and so the additional derivatives of the rotation matrices must be taken into account.

A simple way to include the angular dependency of  $\mathbf{U}_{i\alpha}$  is found by rewriting the global weights in terms of the matrix elements in the local frame,

$$\mathbf{w}_{i\alpha}^{(gl)} = \left[ \frac{1}{2} \left( w_{i\alpha}^\uparrow + w_{i\alpha}^\downarrow \right) \mathbf{1} + \frac{1}{2} \left( w_{i\alpha}^\downarrow - w_{i\alpha}^\uparrow \right) \mathbf{s}_{i\alpha}^{(l)} \cdot \boldsymbol{\sigma} \right]. \quad (7.31)$$

This holds because the local weights are diagonal in spin-space by our definition of the local moments (an analogous expression holds for the onsite levels). The torque can then be written as

$$\frac{dU_B}{d\mathbf{s}_{k\gamma}^{(l)}} = \sum_{i\alpha} \sum_n \frac{d}{d\mathbf{s}_{k\gamma}^{(l)}} \text{Tr} \left( \mathbf{w}_{i\alpha}^{(l)} \boldsymbol{\mu}_{i\alpha}^{(n,l)} \right) = \sum_{i\alpha} \sum_n \frac{d}{d\mathbf{s}_{k\gamma}^{(l)}} \text{Tr} \left( \mathbf{w}_{i\alpha}^{(gl)} \boldsymbol{\mu}_{i\alpha}^{(n,gl)} \right). \quad (7.32)$$

Applying the product rule and substituting for  $\mathbf{w}_{i\alpha}^{(\text{gl})}$ ,

$$\frac{dU_B}{d\mathbf{s}_{k\gamma}^{(l)}} = \sum_{i\alpha} \sum_n^{n_{\max}} \text{Tr} \left( \mathbf{w}_{i\alpha}^{(\text{gl})} \frac{d\boldsymbol{\mu}_{i\alpha}^{(n,\text{gl})}}{d\mathbf{s}_{k\gamma}^{(l)}} + \frac{d\mathbf{w}_{i\alpha}^{(\text{gl})}}{d\mathbf{s}_{k\gamma}^{(l)}} \boldsymbol{\mu}_{i\alpha}^{(n,\text{gl})} \right) \quad (7.33)$$

$$= \sum_n^{n_{\max}} \sum_{i\alpha} \text{Tr} \left( \mathbf{w}_{i\alpha}^{(\text{gl})} \frac{d\boldsymbol{\mu}_{i\alpha}^{(n,\text{gl})}}{d\mathbf{s}_{k\gamma}^{(l)}} + \frac{1}{2} (w_{i\alpha}^{\downarrow} - w_{i\alpha}^{\uparrow}) \boldsymbol{\sigma} \boldsymbol{\mu}_{i\alpha}^{(n,\text{gl})} \right). \quad (7.34)$$

We may now touch base with Eqn. (7.18) such that

$$\frac{dU_B}{d\mathbf{s}_{k\gamma}^{(l)}} = \frac{1}{2} \left( \text{Tr} \left( \tilde{\boldsymbol{\Theta}}_{k\gamma k\gamma}^{(\text{gl})} \boldsymbol{\sigma} \right) \Delta_{k\gamma} - I_k m_k \mathbf{m}_k + \sum_{i\alpha} \sum_n^{n_{\max}} (w_{i\alpha}^{\downarrow} - w_{i\alpha}^{\uparrow}) \text{Tr} \left( \boldsymbol{\sigma} \boldsymbol{\mu}_{i\alpha}^{(n,\text{gl})} \right) \right), \quad (7.35)$$

where  $\Delta_{k\gamma} = E_{k\gamma}^{\downarrow} - E_{k\gamma}^{\uparrow}$ . The additional contribution to the torque from the dependence of  $\mathbf{U}_{i\alpha}$  on  $\mathbf{s}_{i\alpha}^{(l)}$  is missing from Eqn. (142) of Ref. [17]. Analytic torques would be required for dynamic simulations of iron at finite temperatures if an equation of motion for the spins can be defined.

### 7.3.2 Transverse magnetic moment components

As discussed in section 3.3.4, the direction of the output magnetic moment as calculated from the exact TB diagonalisation will not, in general, point along the input magnetic moment direction used to define the initial Hamiltonian onsite levels. The two directions will only be equal when a self-consistent solution is found. The final magnetic moment direction can, however, be constrained to lie along the initial vector by the application of local orthogonal magnetic fields. In the preceding BOP model, we have neglected the contribution of the transverse components of the output magnetic moment to the energy, and only considered the longitudinal component – the magnitude along the initial direction. Yet, for highly non-collinear structures, the output magnetic moment direction can differ greatly from the input and should be taken into account for an accurate description of the energy and forces.

These transverse components may be determined by rotating the global moments ma-

trix,  $\boldsymbol{\mu}_{i\alpha}^{(p,gl)}$ , into two directions,  $\mathbf{p}_i^{(1)}$  and  $\mathbf{p}_i^{(2)}$ , mutually orthogonal to the local input spin direction, as determined by the Gram-Schmidt process.<sup>121</sup> The choice of these directions is not unique but forms a necessary basis to express the output magnetic moment components in the global coordinate system. The global matrix is rotated into  $\mathbf{p}_i^{(1)}$  and  $\mathbf{p}_i^{(2)}$  according to

$$\boldsymbol{\mu}_{i\alpha}^{(p,\mathbf{p}_a)} = \mathbf{U}_{i\alpha}^{\mathbf{p}_a} \boldsymbol{\mu}_{i\alpha}^{(p,gl)} \mathbf{U}_{i\alpha}^{\mathbf{p}_a \dagger} = \begin{pmatrix} \mu_{i\alpha\mu\uparrow\uparrow}^{(p,\mathbf{p}_a)} & \mu_{i\alpha\mu\uparrow\downarrow}^{(p,\mathbf{p}_a)} \\ \mu_{i\alpha\mu\downarrow\uparrow}^{(p,\mathbf{p}_a)} & \mu_{i\alpha\mu\downarrow\downarrow}^{(p,\mathbf{p}_a)} \end{pmatrix}, \quad (7.36)$$

where  $\mathbf{U}_{i\alpha}^{\mathbf{p}_a}$  is the appropriate transformation matrix. Once again this process does not diagonalise the matrix, but we may use the real diagonal components in a BOP expansion of the up and down DOS in each direction. If identical  $a_{i\alpha}^{(\infty)}$  and  $b_{i\alpha}^{(\infty)}$  are used for each spin band in each of the three directions ( $\mathbf{s}_{i\alpha}^{(l)}$ ,  $\mathbf{p}_{i\alpha}^{(1)}$  and  $\mathbf{p}_{i\alpha}^{(2)}$ ), then the Fermi level which conserves the total number of electrons in each direction will be the same. If, however,  $a_{i\alpha}^{(\infty)}$  and  $b_{i\alpha}^{(\infty)}$  are determined directly from the moments for each band in each direction, there will be three numerically different ‘Fermi levels’ for each direction. The magnitude of the magnetic moment component along each direction is simply the difference between the number of electrons in the up and down channels, as for the longitudinal case.

By analogy to the case of local charge neutrality (see section 4.3.2), the final magnetic moment may be constrained to the initial input direction by adding a term to the energy which depends on the magnitude of the transverse components,

$$U_B = U_{Bond} + U_X + U_C + U_T + U_{Rep}, \quad (7.37)$$

where the transverse energy,  $U_T$ , is given by

$$U_T = \frac{1}{4} \sum_i (I_{i\mathbf{p}_1} m_{i\mathbf{p}_1}^2 + I_{i\mathbf{p}_2} m_{i\mathbf{p}_2}^2). \quad (7.38)$$

The global Hamiltonian onsite elements are adjusted according to

$$\mathbf{E}_{i\alpha} = \mathbf{E}_{i\alpha}^{(z)} + \frac{1}{2} (I_{i\mathbf{p}_1} \mathbf{m}_{i\mathbf{p}_1} + I_{i\mathbf{p}_2} \mathbf{m}_{i\mathbf{p}_2}) \cdot \boldsymbol{\sigma}. \quad (7.39)$$

$\mathbf{E}_{i\alpha}^{(z)}$  is the matrix of onsite levels already containing the shifts due to the longitudinal magnetic moment components and any charge transfer.  $I_{i\mathbf{p}_1}$  and  $I_{i\mathbf{p}_2}$  are positive constants to be increased until the transverse components are numerically zero. This methodology is analogous to that employed in non-collinear DFT codes, except that the BOP energy is minimised directly rather than indirectly by achieving self-consistency in the DFT spin density. Note the difference in signs between the transverse and longitudinal additions to the Hamiltonian and energy. An increase in the longitudinal component lowers the energy due to increased exchange, while an increase in the transverse components leads to a rise in the total energy. These extra terms introduce the derivatives

$$\frac{dU_T}{d\Lambda} = -\frac{1}{2} \sum_{i\alpha\nu} \left( (-1)^\nu I_{i\mathbf{p}_1} m_{i\alpha\mathbf{p}_1} - \frac{\sum_{j\beta\mu} (-1)^\mu I_{j\mathbf{p}_1} m_{j\beta\mathbf{p}_1} n_{j\beta\mu}(E_F)}{\sum_{j\beta\mu} n_{j\beta\mu}(E_F)} \right) \quad (7.40)$$

$$+ (-1)^\nu I_{i\mathbf{p}_2} m_{i\alpha\mathbf{p}_2} - \frac{\sum_{j\beta\mu} (-1)^\mu I_{j\mathbf{p}_2} m_{j\beta\mathbf{p}_2} n_{j\beta\mu}(E_F)}{\sum_{j\beta\mu} n_{j\beta\mu}(E_F)} \int^{E_F} \frac{dn_{i\alpha\nu}(E)}{d\Lambda}, \quad (7.41)$$

which must be included in the weights, Eqn. (7.20).

The local weights along  $\mathbf{p}_i^{(1)}$  and  $\mathbf{p}_i^{(2)}$  must be rotated back into the global coordinate system with the appropriate transformation matrices before the evaluation of the gradients using Eqn. (7.22).

## 7.4 Implementation in BOPfox

The analytic BOP method for non-collinear magnetic configurations was implemented as part of this work into the existing BOPFOX code. The subroutines for the calculation of the local weights could be reused from the collinear code. The general spin-space rotations were added and the routines for the calculation of the interference paths, moments,

transfer paths and bond-order were substantially rewritten to take account of the complex variables as well as the matrix forms and operations.

The flow of a non-collinear BOP calculation is illustrated in Figure 7.1. The Hamiltonian matrix is set up in the global frame where the moments of the local DOS are also calculated. The moments are rotated into the local frame and a BOP expansion is performed for the local up- and down-spin channels, neglecting the off-diagonal elements of the moments matrix. The derivatives which define the  $\uparrow$  and  $\downarrow$  weights are calculated locally before rotating back into the global space. This process is repeated for the two transverse directions orthogonal to the input magnetic moment. The transfer paths and bond-order are constructed in the global frame from the weights and the interference paths. The bond-order is rotated back into the local frame so that the gradients of the energy with respect to the local onsite levels may be evaluated. The same mixing scheme as for collinear BOP (see section 4.4) uses the gradients to update the onsite levels which are then rotated back into the global Hamiltonian, the entire process being repeated until the gradients are numerically zero. At this stationary point in the energy the forces on the atoms and torques on the spins may be calculated from the bond-order.

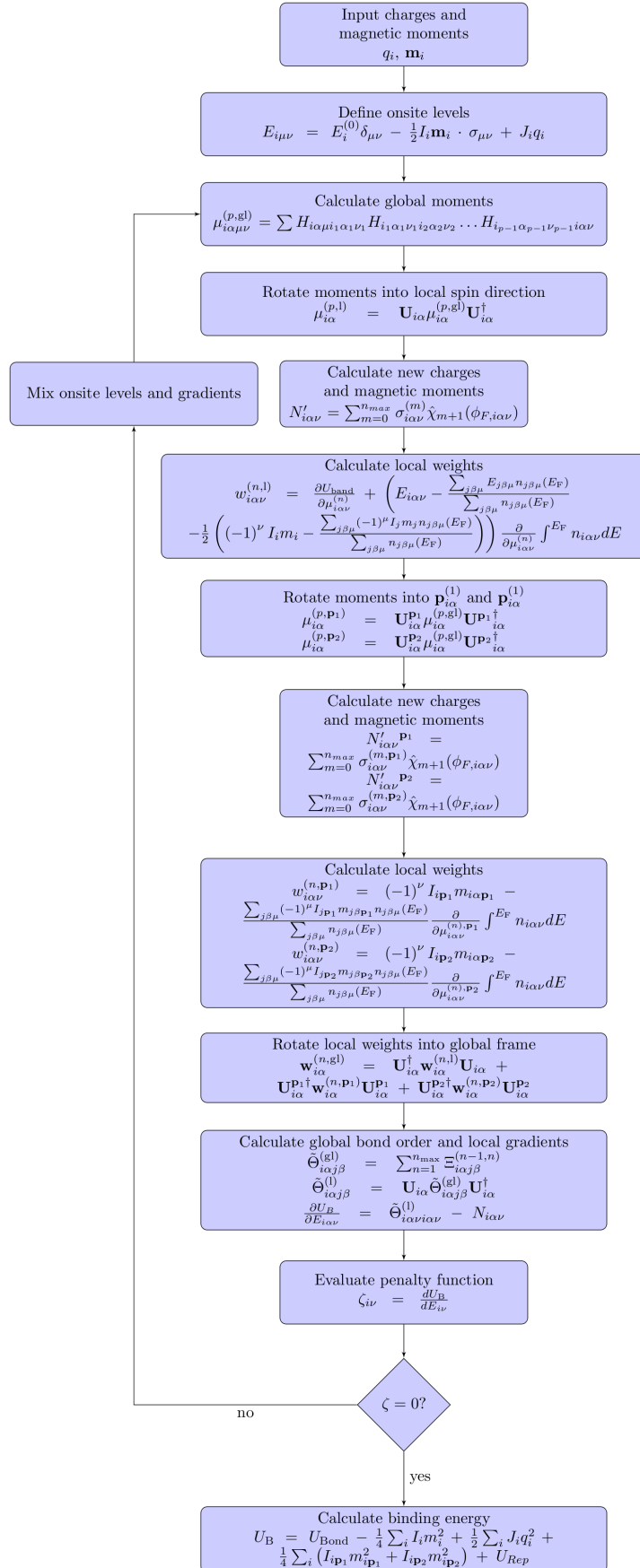


Figure 7.1: Schematic flowchart illustrating the energy minimisation procedure for a non-collinear magnetic analytic BOP calculation including gradients derived from the transverse components of the magnetic moments.

## 7.5 Simple non-collinear structures

### 7.5.1 Transverse magnetic moment components

As explained in section 7.3.2, the output magnetic moments calculated from the eigenvalues of a TB diagonalisation are only equal to the input magnetic moments, used to define the onsite levels, at self-consistency. The calculation of the components of the output magnetic moment orthogonal to the input moment direction is necessary for constrained magnetic calculations (see section 3.3.4). Similarly, by performing the BOP expansion in the two locally rotated directions,  $\mathbf{p}_{i\alpha}^{(1)}$  and  $\mathbf{p}_{i\alpha}^{(2)}$ , these transverse components of the magnetic moments may be approximated in the same manner as for the longitudinal components along  $\mathbf{s}_{i\alpha}^{(1)}$ . For small angles between adjacent moments, these transverse components are also small, as are their contributions to the binding energy and gradients. For highly non-collinear structures, however, their contributions can be quite large. The reproduction of such moments is an initial test of the accuracy of the non-collinear approximation used in analytic BOP.

| Input spin vector | TB output vector | BOP+ output vector |
|-------------------|------------------|--------------------|
| [0 0 2]           | [0.00 0.00 2.35] | [0.00 0.00 2.37]   |
| [0 0 2]           | [0.00 0.00 2.35] | [0.00 0.00 2.37]   |
| [0 1 2]           | [0.00 1.07 2.29] | [0.00 1.10 2.38]   |
| [0 0 2]           | [0.00 0.07 2.32] | [0.00 0.11 2.43]   |
| [0 2 0]           | [0.00 2.26 0.35] | [0.00 2.37 0.43]   |
| [0 0 2]           | [0.00 0.35 2.26] | [0.00 0.44 2.37]   |
| [2 0 0]           | [2.26 0.00 0.35] | [2.37 0.00 0.44]   |
| [0 0 2]           | [0.35 0.00 2.26] | [0.44 0.00 2.37]   |

Table 7.1: Pairs of magnetic moment vectors calculated by non-self-consistent TB and 9-moment analytic BOP+, and the corresponding input magnetic moment used to construct the Hamiltonian. Calculations for 2-atom bcc cell.

In Table 7.1 the output magnetic moment vectors from one non-self-consistent TB

diagonalisation are compared to the input vectors used to construct the onsite levels in a bcc simulation cell containing two atoms. The vectors are written as components along the Cartesian axes as  $[x\ y\ z]$ . These are also compared to the corresponding 9-moment analytic BOP+ magnetic moments calculated from the same Hamiltonian. For collinear calculations, the transverse components are always zero as demanded by the symmetry of the structure. For the non-collinear calculations, however, the BOP is able to reproduce qualitatively the output magnetic moments of TB. By fixing the orientation of the magnetic moment on the second atom to lie along the z-axis in each structure, it is easy to see how the presence of the canted moment on the first atom induces a transverse component to the output moment. The analytic BOP is able to reproduce the magnetic moments to within  $0.1\ \mu_B$ .

### 7.5.2 Rotation from FM to AFM

As seen in section 7.5.1, the two-atom bcc cell is the simplest possible simulation supercell of Fe where non-collinear magnetic states can be investigated. The angle of the spins on each atom can be rotated between  $0^\circ$  (FM) and  $180^\circ$  (AFM), and one would expect the magnetic moments and energy to vary continuously. Such a simple arrangement has already been investigated by Drautz & Pettifor<sup>17</sup> within a fourth-moment approximation.

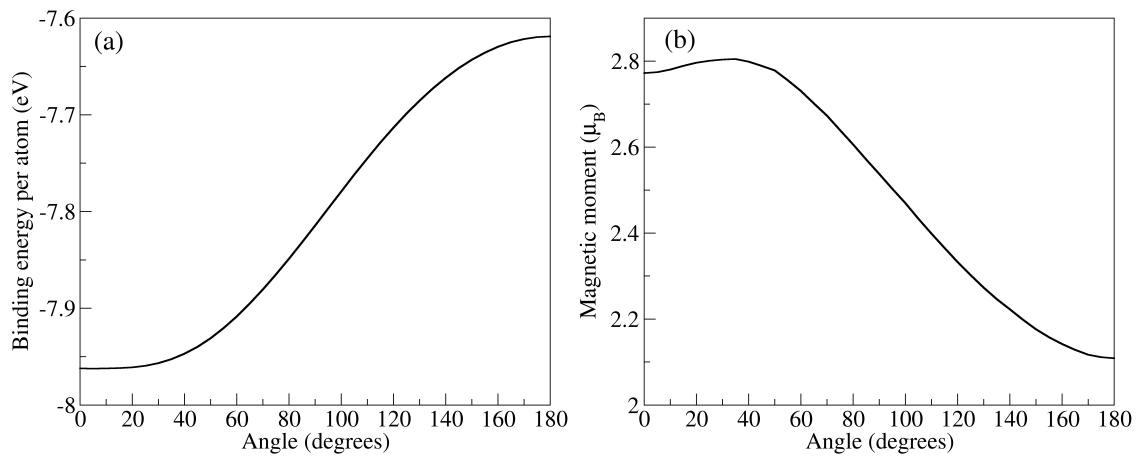


Figure 7.2: (a) Binding energy per atom and (b) magnetic moment as a function of rotation angle between spin directions in a 2-atom bcc iron cell as calculated with TB.

The fourth moment of the DOS is the first that leads to a direct geometrical interaction of magnetic moments on neighbouring sites, since it is the first to combine onsite hops on both atoms. The fourth moment also shows a Heisenberg-like  $\cos \theta$  dependence on the angle between spin directions,  $\theta$ . If the magnetic moments are frozen in magnitude as the spin directions are rotated, then the bond energy also shows a Heisenberg-like dependency on the spins. The simple Heisenberg description for the energy is then predicted by the fourth-moment TB model, but higher moment contributions continue to modify this. In realistic situations where the magnitude of the magnetic moment depends on the relative spin orientation, the Heisenberg model is not found to be accurate, and higher-moment multispin interactions become important.<sup>17</sup>

In Fig. 7.2 (a), the self-consistent TB binding energy per atom is plotted as a function of the angle between magnetic moments in the 2-atom bcc unit cell. The corresponding magnetic moment is plotted in (b). The magnetic moment exhibits a maximum value at  $35^\circ$  before decreasing to a minimum value at antiferromagnetic alignment. The overall binding energy does not have a stationary point, however, at  $35^\circ$ .

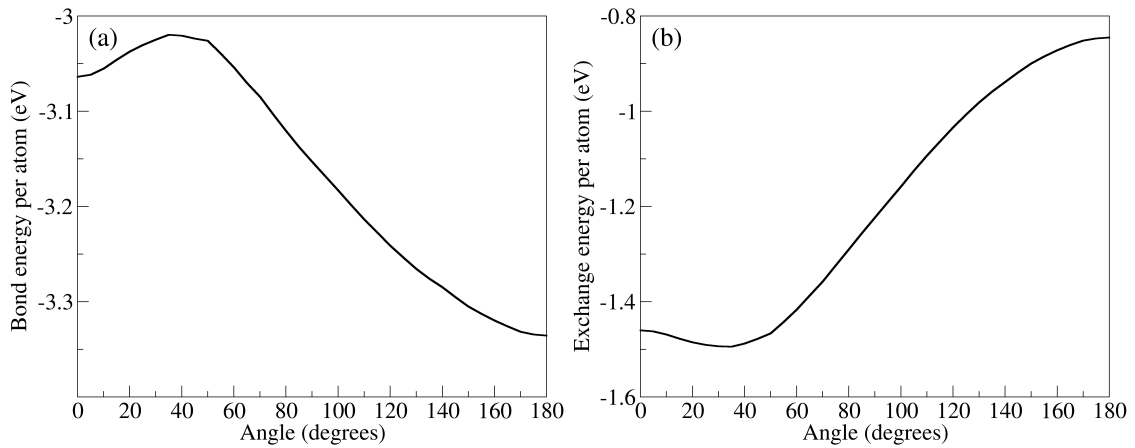


Figure 7.3: (a) Bond energy per atom and (b) exchange energy per atom as a function of rotation angle between spin directions in a 2-atom bcc iron cell as calculated with TB.

The electronic portion of the binding energy is broken down further into bond and exchange contributions in Fig. 7.3. The bond energy is at a maximum when the magnetic moment is at its highest value, whereas the exchange energy is at a minimum. Thus

the change in the binding energy is in fact due to a cancellation between the bond and exchange contributions, leading to an overall monotonic increase in the energy.

The binding energy, however, *does* show a shallow minimum at a rotation of  $6^\circ$  (see Fig. 7.4). This minimum does not seem to be associated with any discernible change in the magnetic moment, bond energy or exchange energy. This means that for the 2-atom bcc cell, the TB magnetic ground state is non-collinear rather than ferromagnetic, which is clearly unphysical. These results – both the maximum in the magnetic moment at  $35^\circ$  and the non-collinear ground state at  $6^\circ$  – are most likely artefacts of the particular TB model, but are also consistent with the known result that *sp* and *d* hybridisation is required to achieve an accurate value for the spin-wave stiffness constant. Indeed,  $D$  is found to be negative for other TB *d*-only parametrisations, as it is here.

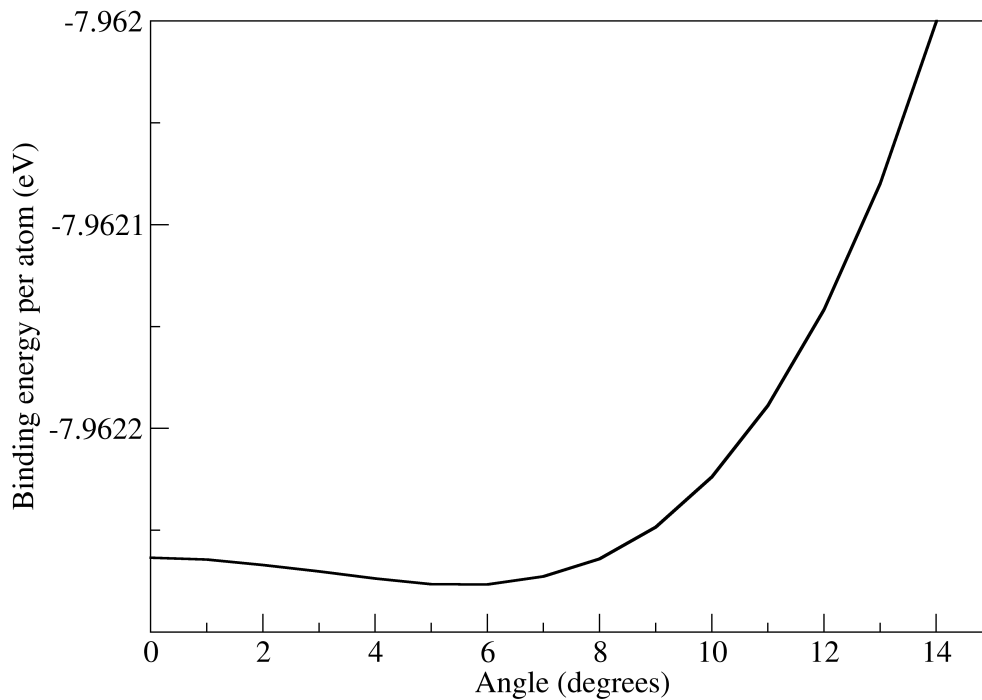


Figure 7.4: TB binding energy per atom as a function of rotation angle between spin directions in a 2-atom bcc iron cell.

The corresponding 9-moment BOP and BOP+ energies are plotted as a function of

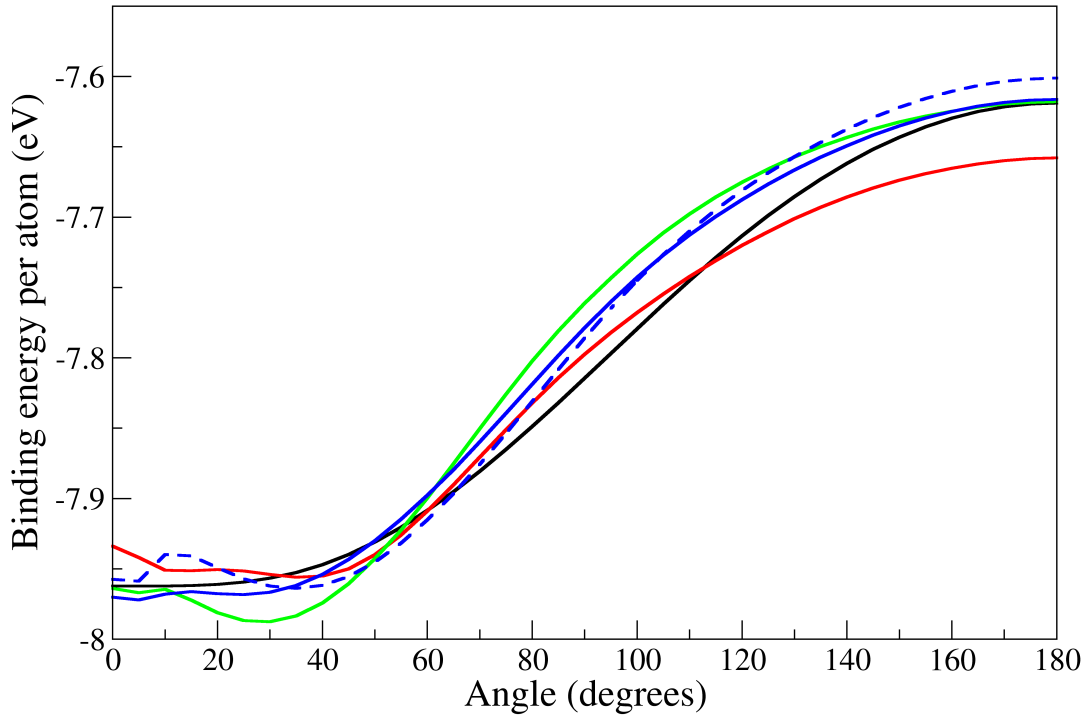


Figure 7.5: TB, BOP and BOP+ binding energy per atom as a function of rotation angle between spin directions in a 2-atom bcc iron cell. TB is marked black, 9-moment BOP red, 9-moment BOP+ (maximum bandwidth) in green, 9-moment BOP+ (Gershgorin) in blue and 9-moment BOP+ (modified Gershgorin) in dashed blue.

rotation angle in Fig. 7.5. The standard analytic BOP method (red) shows the worst fit to the TB result (black), and also presents two local energy minima at  $15^\circ$  and  $35^\circ$ . The BOP+ results are much closer to TB, particularly towards antiferromagnetic alignment, but still show curious behaviours for low-angle rotations. With  $a^{(\infty)}$  and  $b^{(\infty)}$  defined by the maximum possible bandwidth, according to Eqn. (4.87) and (4.88), the energy shows a deep non-collinear minimum at  $30^\circ$ . The fit using  $a^{(\infty)}$  and  $b^{(\infty)}$  defined by Gershgorin's theorem is much closer to TB, but there are still local minima at  $5^\circ$  and  $25^\circ$ . A third possibility is also included, where we separate the calculation of  $a^{(\infty)}$  and  $b^{(\infty)}$ , used to define the bandwidth, from the constant values used to determine the additional moments in the BOP+ method beyond  $m_{\text{rec}}^{\text{max}}$  (see section 4.3.4). In this case Gershgorin's theorem is used to determine the  $a^{(\infty)}$  and  $b^{(\infty)}$  for the bandwidth, but the additional moments are

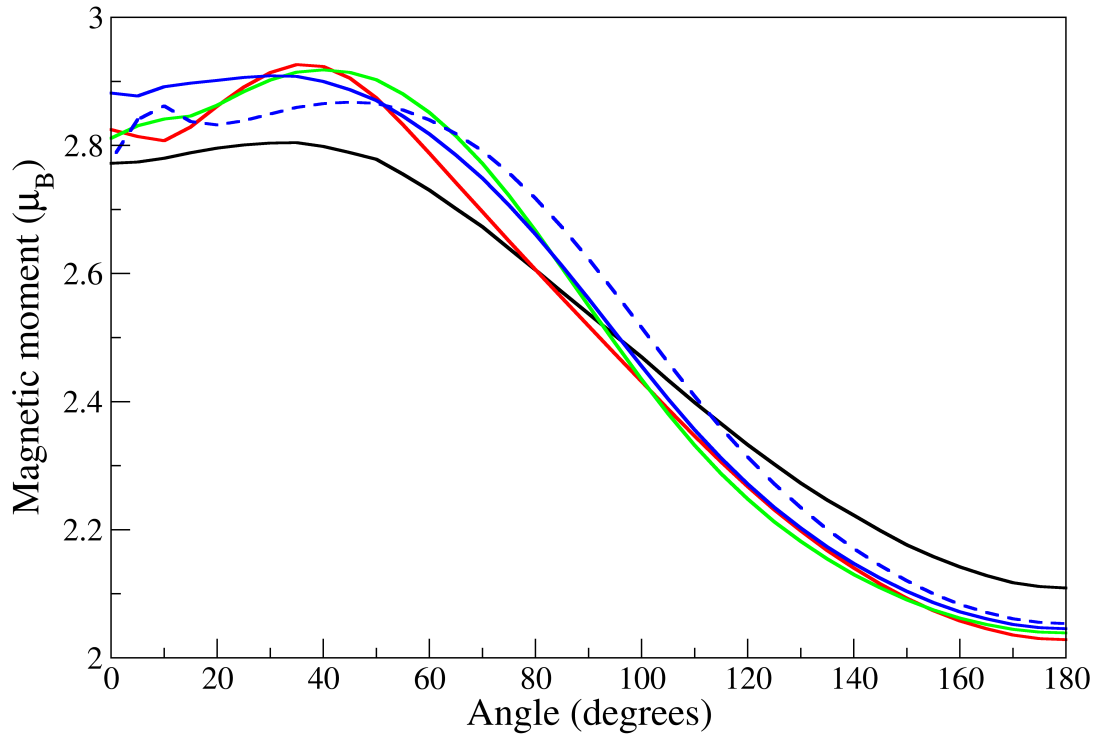


Figure 7.6: TB, BOP and BOP+ magnetic moments as a function of rotation angle between spin directions in a 2-atom bcc iron cell. TB is marked black, 9-moment BOP red, 9-moment BOP+ (maximum bandwidth) in green, 9-moment BOP+ (Gershgorin) in blue and 9-moment BOP+ (modified Gershgorin) in dashed blue.

calculated using the running averaged definitions, Eqn. (4.73) and (4.74) – this is referred to as the modified Gershgorin method in Fig. 7.5. Once again we find there is a problem for low-angle rotations.

The smooth variation of the TB energy as a function of rotation is a result of a cancellation between the bond and exchange energies. In Fig. 7.6, the 9-moment BOP and BOP+ magnetic moments are plotted as a function of rotation. While for rotations of  $50^\circ$  and beyond, where the magnetic moments vary smoothly, the behaviour at low angles can be qualitatively incorrect. Even for 9-moment BOP+ with the Gershgorin  $a^{(\infty)}$  and  $b^{(\infty)}$ , where the qualitative behaviour of the magnetic moments is similar to TB, an inaccuracy of only  $0.1 \mu_B$  is enough to destroy the delicate balance between bond and exchange energies. It is clear that the precise behaviour of the TB magnetic moments must

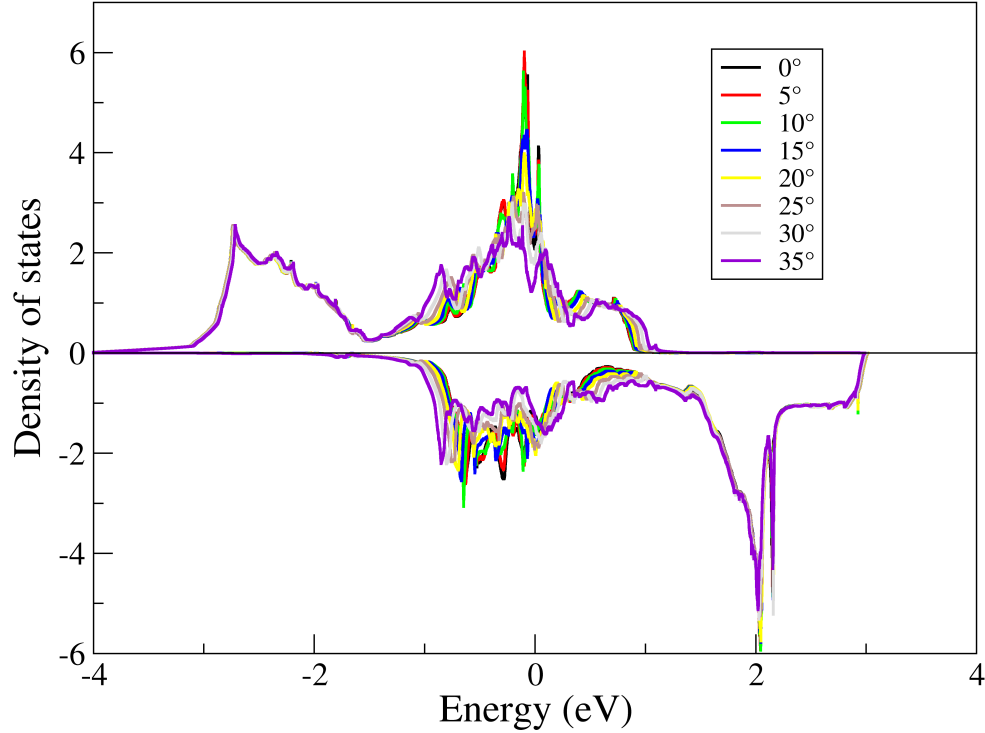


Figure 7.7: TB majority (positive) and minority (negative) local DOS projected along the local spin direction, as a function of rotation angle between spin directions on adjacent sites in a 2-atom bcc iron cell. The two sites remain equivalent due to the neglect of spin-orbit coupling.

be reproduced accurately in order for the behaviour of the energy to be even qualitatively correct.

Fig. 7.7 shows the spin-polarised TB local DOS as a function of rotation angle between  $0^\circ$  and  $35^\circ$ . What is striking is how stable the DOS appears to be for small rotations of the spins. Large sections of both the majority and minority spin DOS barely change, right up to  $35^\circ$ . The majority of the change is located in the upper peak of the majority band and the lower region of the minority band. Even here, however, the changes for very small rotations of the order of  $5^\circ$  to  $10^\circ$  are weak and it is hard to describe a general behaviour, such as a continuous reduction in peak height. This stability of the main features of the

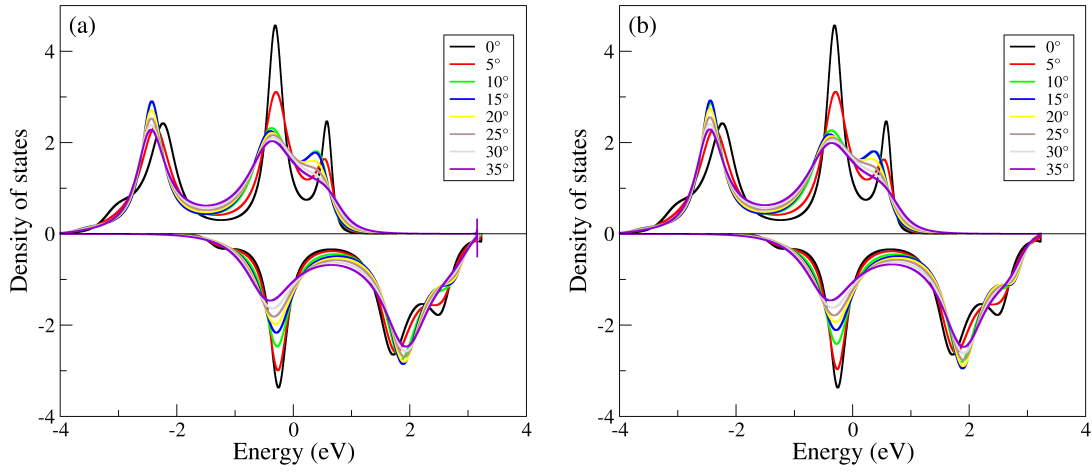


Figure 7.8: 9-moment BOP+ majority (positive) and minority (negative) local DOS calculated as a function of rotation angle between spin directions in a 2-atom bcc iron cell using (a) Gershgorin's  $a^{(\infty)}$  and  $b^{(\infty)}$  and (b) constant  $a_{\text{FM}}^{(\infty)}$  and  $b_{\text{FM}}^{(\infty)}$ .

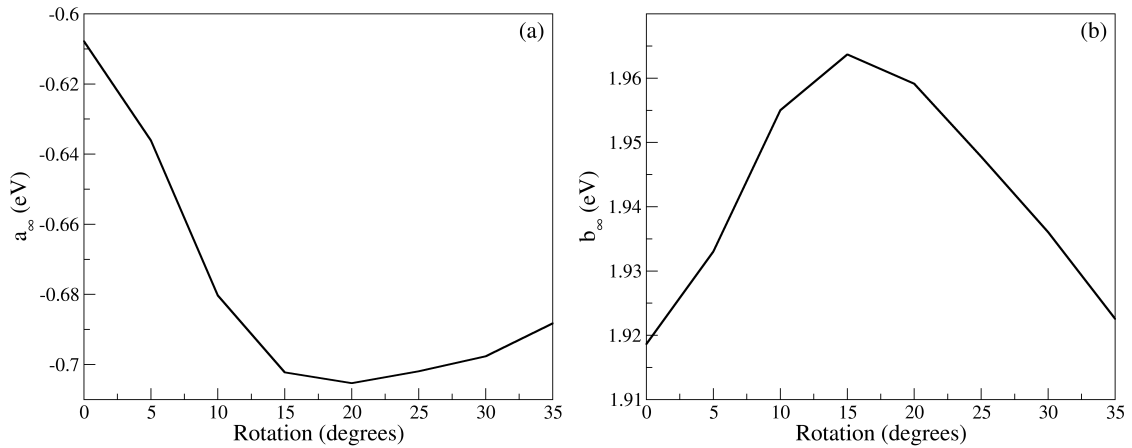


Figure 7.9: Variation of Gershgorin's (a)  $a^{(\infty)}$  and (b)  $b^{(\infty)}$  as a function of rotation angle between spin directions in a 2-atom bcc iron cell as calculated by 9-moment BOP+.

TB DOS implies that any major changes of shape as a function of spin rotation involve higher moment contributions. The precise behaviour of the energy is clearly dependent on these subtle changes in the DOS.

The corresponding non-self-consistent 9-moment BOP+ DOS is shown in Fig. 7.8 (a). The BOP+ DOS does not show the same stability under rotation of the spin directions as the TB DOS. One reason for this might be the variation of the bandwidth, defined by  $a^{(\infty)}$  and  $b^{(\infty)}$ , with spin direction. Fig. 7.9 shows how the Gershgorin  $a^{(\infty)}$  and

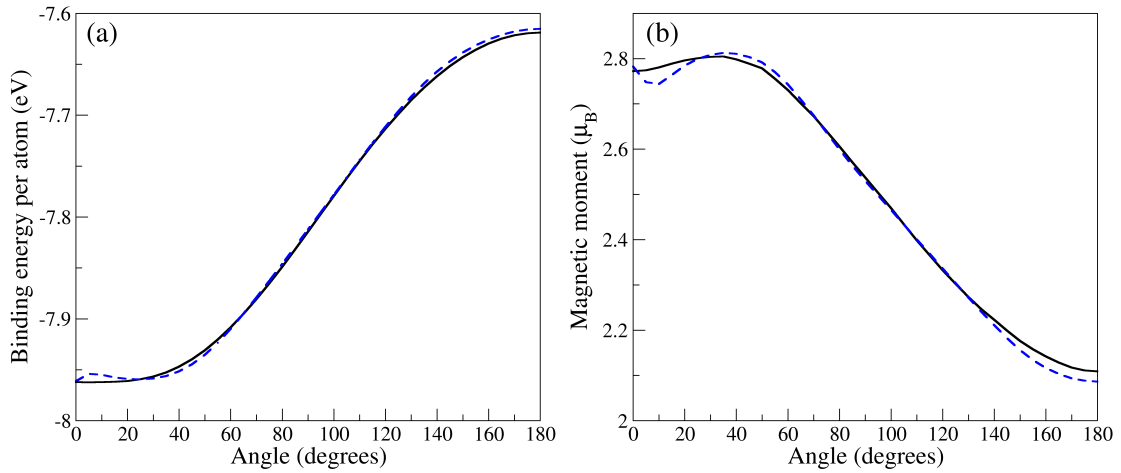


Figure 7.10: (a) Binding energy per atom and (b) magnetic moment as a function of spin rotation angle in a 2-atom bcc cell as calculated with TB in black and 16-moment BOP+ (modified Gershgorin) in dashed blue.

$b^{(\infty)}$  corresponding to the DOS in Fig. 7.8 change on rotation; they are certainly not constant for low-angle rotations (as the TB DOS might superficially suggest). However, fixing  $a^{(\infty)}$  and  $b^{(\infty)}$  throughout the rotation to constant values calculated for the purely FM configuration,  $a_{\text{FM}}^{(\infty)}$  and  $b_{\text{FM}}^{(\infty)}$ , does not improve the stability of the BOP DOS. In fact, the shape of the DOS is barely changed (see Fig. 7.8 (b)). The implication is that the incorrect behaviour of the BOP DOS for low-angle rotations is not an effect of the particular approximation for the bandwidth, but is due to the neglect of higher moment contributions to the DOS shape. Nevertheless, it remains a possibility that a terminator with an explicit dependence on the local magnetic environment could be used to circumvent this problem.

Indeed, increasing the number of moments in the BOP expansion does improve the resolution of the energy. In Fig. 7.10 the 16-moment BOP+ energy and magnetic moments are plotted as calculated using the modified Gershgorin method. In this case the agreement with TB is much better throughout the rotation, a result of an improved fit to the TB DOS (see Fig. 7.11). However, the behaviour of the magnetic moment, and hence energy, is still incorrect below  $20^\circ$ . This observation is consistent with previously

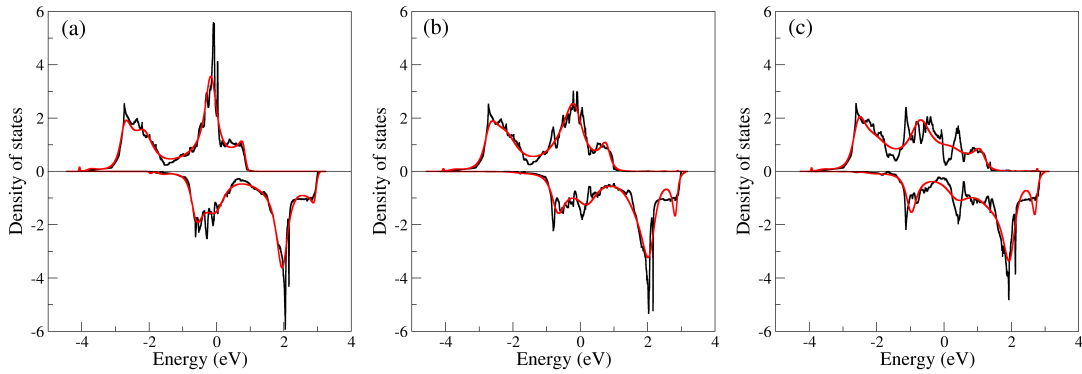


Figure 7.11: TB (black) and 16-moment BOP+ majority (positive) and minority (negative) spin-polarised DOS for 2-atom bcc iron cell with spins at (a)  $0^\circ$ , (b)  $30^\circ$  and (c)  $60^\circ$ .

published recursion method results and the elastic constants calculated in section 5.3.4. For example, Luchini & Heine<sup>167</sup> had to use a minimum of 90 recursion levels (180 moments) in order to calculate the long-wavelength spin-wave stiffness constant accurately. The behaviour of the stiffness constant, like the elastic constants, depends critically on the fine detail of the electronic structure near the Fermi surface. This makes a real-space calculation particularly difficult. While low numbers of moments can reproduce the broad behaviour (for example 4 moments are sufficient to drive the general increase in energy from FM to AFM alignment), significantly more are necessary to resolve the fine details.

### 7.5.3 Single spin rotation

Another interesting non-collinear test case to consider is the rotation of a single spin in bcc Fe. For these calculations a 16-atom ferromagnetic supercell was used and the magnetic moment on one atom was rotated between ferromagnetic and antiferromagnetic alignment with the ‘bulk’.

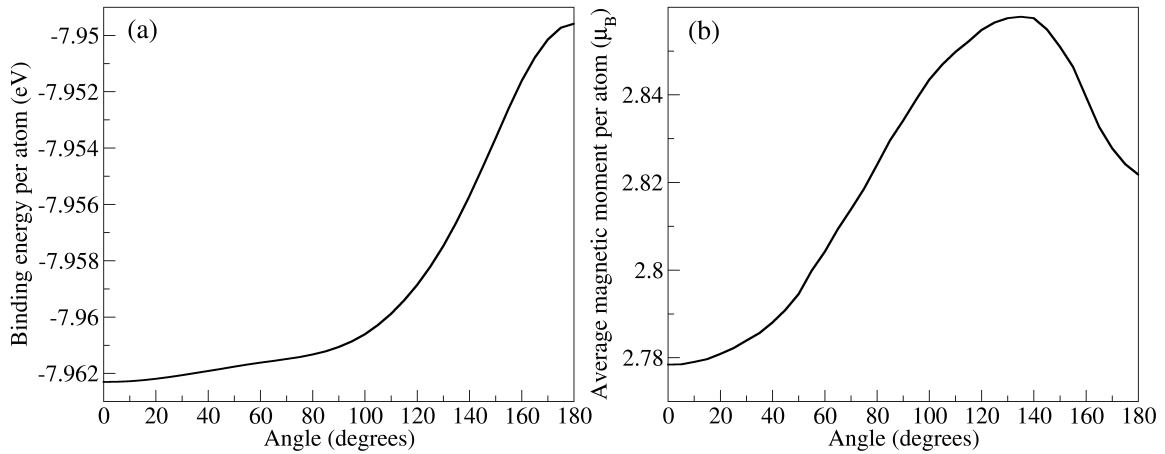


Figure 7.12: Calculation for rotating the spin direction on one atom in 16-atom FM bcc supercell. (a) Self-consistent TB binding energy per atom and (b) magnitude of average magnetic moment per atom as a function of rotation angle.

The TB binding energy per atom and magnitude of the average self-consistent magnetic moment per atom are plotted as a function of the rotation angle in Fig. 7.12. The energy of the system increases continuously as the moment is rotated and the minimum energy configuration is ferromagnetic – there is no spurious non-collinear ground state as found in the 2-atom cell. While the local magnetic moment on the atom in question decreases in magnitude as it is rotated from FM to AFM alignment, the average moment per atom passes through a maximum at a rotation of  $135^\circ$ . So although the rotated moment must decrease in length, the magnetic moments on the surrounding atoms are able to expand. This is reflected by a maximum in the bond energy and a minimum in the exchange energy as seen in Fig. 7.13. Once again, the monotonic behaviour of the total binding energy depends on the cancellation of competing changes in the bond and

exchange energies.

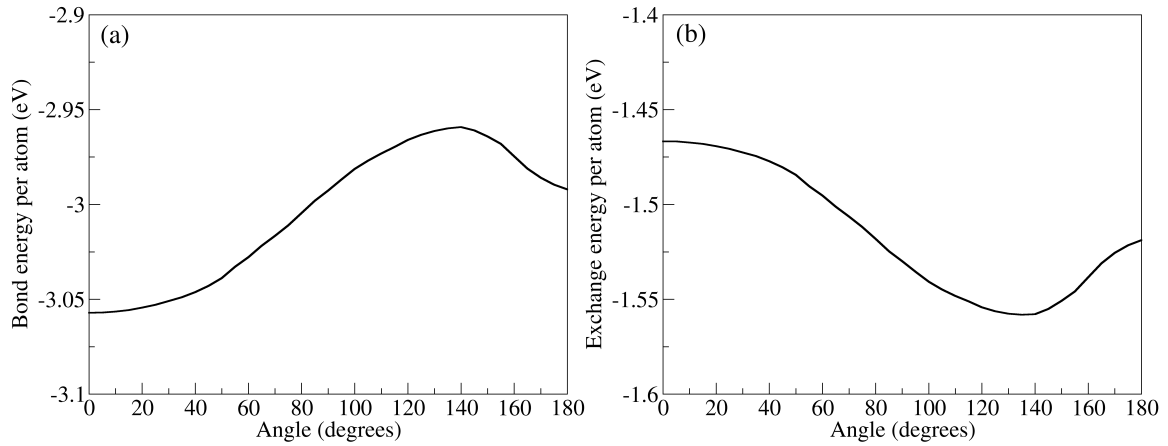


Figure 7.13: Calculation for rotating the spin direction on one atom in 16-atom FM bcc supercell. (a) Self-consistent TB bond energy per atom and (b) exchange energy per atom as a function of rotation angle.

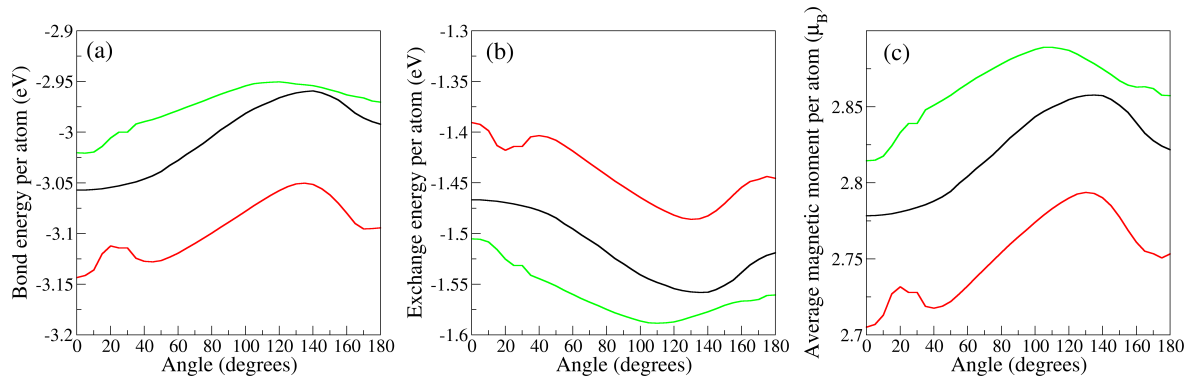


Figure 7.14: (a) Bond energy per atom, (b) exchange energy per atom and (c) average magnetic moment per atom as a function of rotation angle for a single spin in a 16-atom bcc cell. TB results are in black, 9-moment BOP in red and 9-moment BOP+ (maximum bandwidth) in green.

The corresponding bond and exchange energies, as well as average magnetic moments, as calculated with 9-moment BOP and BOP+, are plotted in Fig. 7.14. These are the result of a single BOP calculation from the self-consistent TB onsite levels (that is to say, the BOP energy has not been minimised). While the behaviour of the magnetic moments in all three cases (TB, BOP and BOP+) is broadly the same, BOP tends to underestimate the TB moment while BOP+ leads to an overestimation. The precise locations of the

maximum averaged magnetic moment are shifted, and the behaviour at very low moments, as for the 2-atom bcc cell, is once again slightly strange. Since the total binding energy depends on a balance of the bond and exchange contributions, the overall shapes of the 9-moment BOP and BOP+ binding energy curves will be completely different from TB.

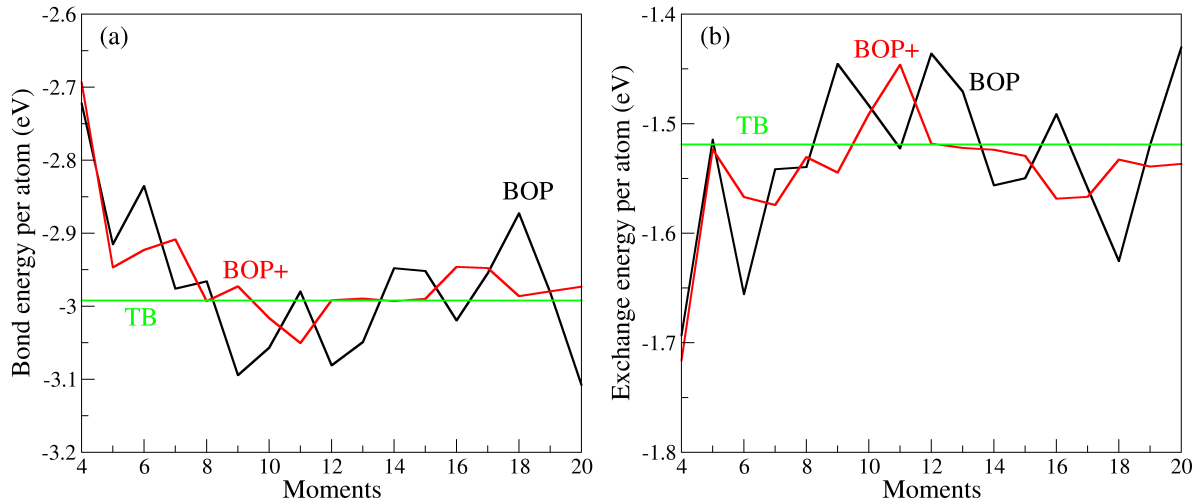


Figure 7.15: Non-self-consistent (a) bond and (b) exchange energies per atom as a function of number of moments for BOP (black) and BOP+ (red) expansions using self-consistent TB onsite levels for an AFM defect in a 16-atom FM bcc cell (TB energies marked in green).

These curves do not take into account the fact that charge transfer is also possible in the 16-atom cell, where the atoms are no longer equivalent. The BOP/BOP+ calculations actually show very large amounts of local charge transfer – up to 0.4 electrons per atom – whose Coulombic contribution would distort the energy profile even further. Taking the collinear antiferromagnetically aligned ‘defect’ in the FM bcc bulk as an example, the convergence of the non-self-consistent bond and exchange energies with the number of moments is shown in Fig. 7.15. The corresponding charge transferred to the defect atom is plotted in Fig. 7.16. The local charges do not converge to zero over this range of moments (although the onsite levels correspond to an LCN TB self-consistent solution).

The 16-moment BOP, BOP+ and TB local DOS on the defect atom and its first nearest neighbour are shown in Figures 7.17 and 7.18 respectively. The TB local DOS on

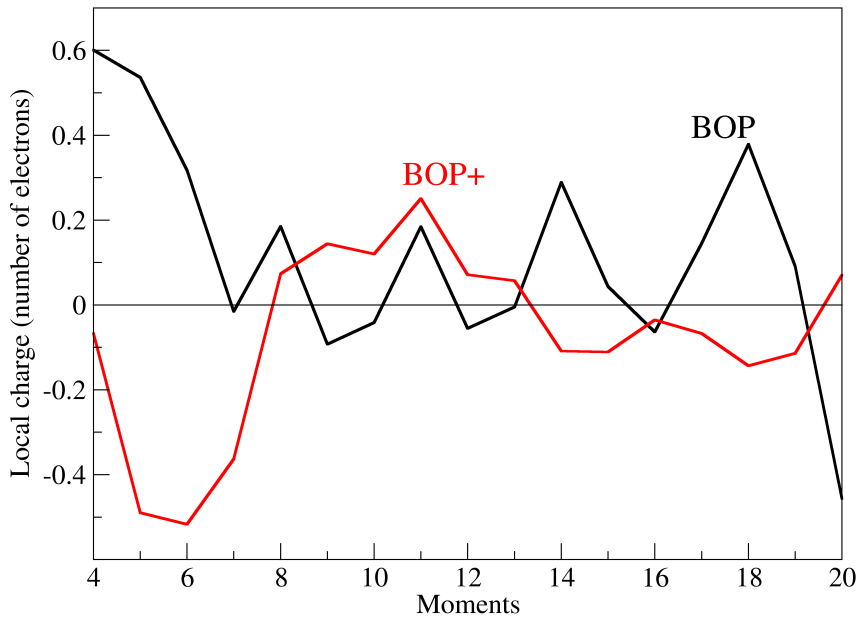


Figure 7.16: Non-self-consistent charge transferred to AFM defect atom in 16-atom FM bcc cell as a function of number of moments for BOP (black) and BOP+ (red) expansions using self-consistent TB onsite levels.

the defect is extremely skewed and almost resembles two delta functions. The 16-moment BOP therefore shows strong oscillations and regions of negative density throughout the band. Additional peaks induced in the TB DOS on the neighbouring atom also lead to quite large regions of negative BOP DOS. The 16-moment BOP+ corrects the problem of negative DOS, yet still is unable to resolve all of the relevant features, particularly the sharp peak in the minority spin band on the defect atom at the Fermi level (the zero of the energy scale).

It seems that for such low-moment expansions, the band-filling properties of the BOP are clearly not accurate enough to reproduce the local magnetic moments or charges of the self-consistent TB model, leading to inaccuracies in the bond and exchange energies of the order of tens of meV. This again indicates that BOP simulations of non-collinear structures would require a specific parametrisation.

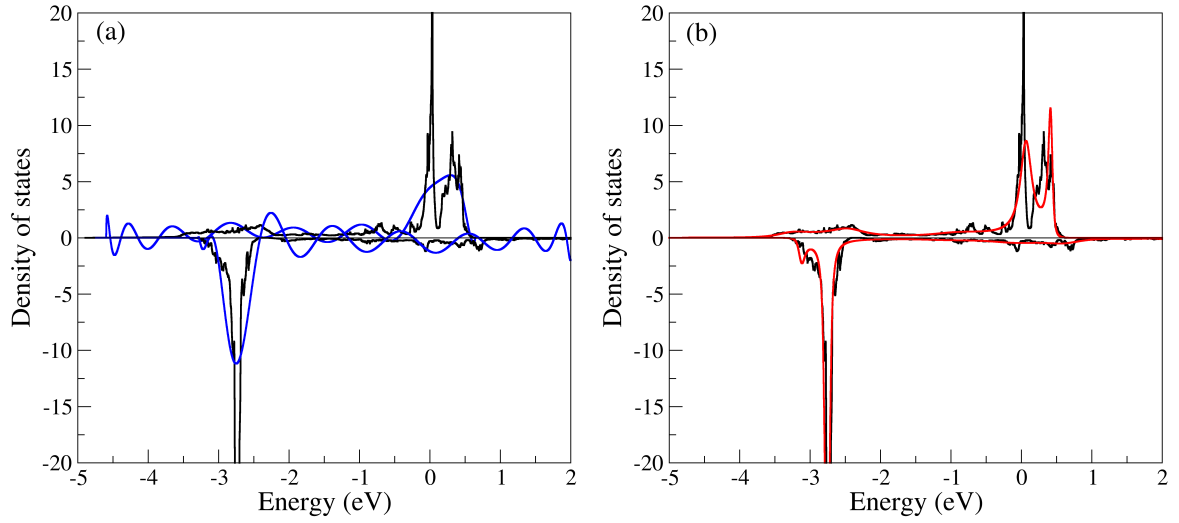


Figure 7.17: Local DOS on the AFM defect atom in 16-atom FM bcc cell calculated with 16-moment (a) BOP (blue) and (b) BOP+ (red). TB DOS is included in black.

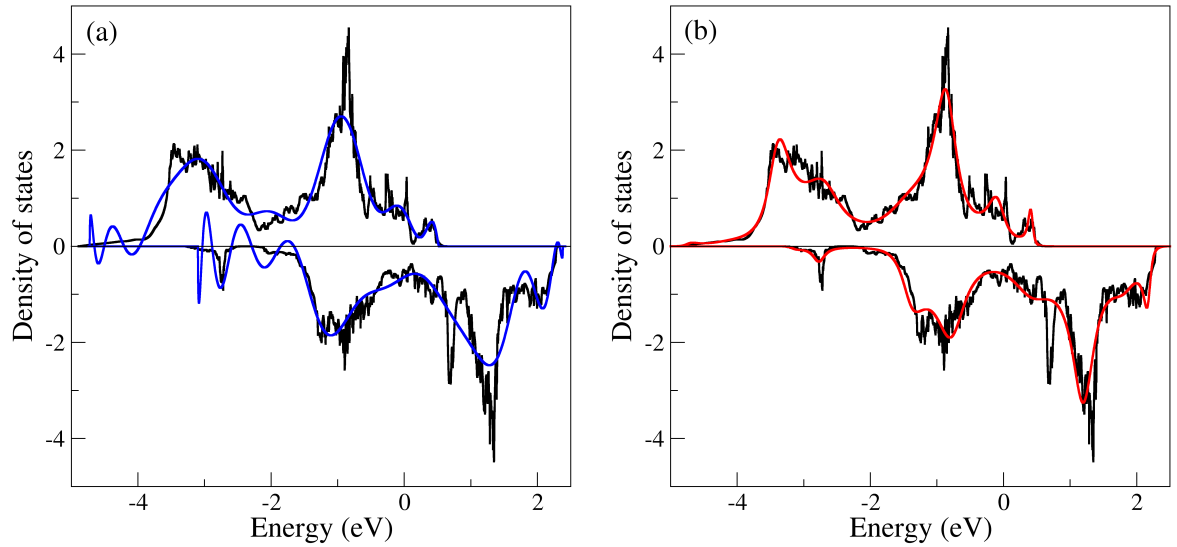


Figure 7.18: Local DOS on first nearest neighbour to the AFM defect atom in 16-atom FM bcc cell calculated with 16-moment (a) BOP (blue) and (b) BOP+ (red). TB DOS is included in black.

## 7.6 Summary

The published theory of the analytic BOPs for non-collinear magnetic configurations has been extended to take into account the necessary rotations between the global spin space and the local spin space aligned with the magnetic moment on each atom. Matrix expressions for the gradients, forces and torques have been introduced which are numerically exact derivatives of the binding energy. A method for calculating the transverse components of the output magnetic moments, dependent on the off-diagonal elements of the TB spin density matrix, has been developed which allows constrained non-collinear calculations to be performed by analogy with the constrained self-consistent TB and DFT methods. These expressions have been implemented in the BOPFOX package.

For the simplest non-collinear bulk structure, the two-atom bcc cell, the non-self-consistent analytic BOP is able to reproduce the TB magnetic moments, from the TB self-consistent onsite levels, to within  $0.1 \mu_B$ . The binding energy of the cell was investigated as a function of the relative angle between spin directions on the two sites. The TB binding energy shows two peculiar phenomena. First, the particular TB model exhibits a non-collinear ground state with the spins canted by  $6^\circ$ . Second, the subsequent monotonically increasing nature of the binding energy is the result of a cancellation between bond and exchange terms, since the magnetic moment passes through a maximum at  $35^\circ$ . The poor description at low-angle spin rotations is a general property of  $d$  TB models. An accuracy of  $0.1 \mu_B$  in the 9-moment BOP magnetic moments is not enough to reproduce the delicate balance of energies. The result is that the BOP often leads to a non-collinear groundstate of relatively large spin misalignments.

The TB DOS appears to be very stable against small rotations of the spins and any changes in the bandfilling behaviour seem to be driven by higher moments of the distribution. Even with 16 exact moments, the BOP+ is unable to reproduce the exact shape of the TB energy curve for small angles, despite the qualitatively good fit of the local DOS and the numerically accurate binding energy between orientations of  $30^\circ$  and  $180^\circ$ .

The rotational properties of a single moment in a 16-atom FM bcc cell were also investigated. While the TB energy and magnetic moments change smoothly as a function of rotation, this is once again the result of a cancellation between bond and exchange terms. The BOP methods cannot reproduce the behaviour of the magnetic moments, and the variation of the bond and exchange energies is much worse than for the 2-atom case. Local charge transfer becomes a possibility in this cell and it seems that the BOP charges around the defect do not converge quickly to the LCN TB values. An accurate BOP model for use in non-collinear calculations such as this would require a specific parametrisation taking into account the predicted charge transfer in the fitting procedure.

# Chapter 8

## Summary and conclusion

It is clear that the development of a transferable interatomic potential for iron is challenging. The particular bulk, defect and interface crystal structures taken by iron and steel alloys are determined by the complex interplay between partially localised  $d$  electron states and the more delocalised  $s$  and  $p$  electrons. This leads to a particular combination of both local and itinerant magnetic properties, which are difficult to describe accurately within 0K electronic structure theory, let alone with a simplified interatomic potential. The finite-temperature mechanical behaviour of iron is also tied to its magnetic structure, especially the entropic contributions of fluctuating, thermally disordered (i.e. non-collinear) local magnetic moments. While the static, 0K structures are described relatively well by *ab initio* methods (with the appropriate choice of exchange-correlation potential), the existing interatomic potentials, which are required for really large-scale or dynamic simulations, seem inadequate. The magnetic analytic BOP method is a next step in moving beyond the constraints of the common Embedded Atom Method towards a more realistic description of magnetic iron in dynamic simulations.

By expanding a reference semi-elliptic density of states function in terms of the exact moments of the TB DOS, the TB distribution itself can, in theory, be approached. This allows for the derivation of analytic expressions for the band-filling, magnetic moments, energy and forces which may be evaluated quickly in comparison to exact TB diagonal-

isation methods. Previously, the magnetic analytic BOP has only been tested for very simple bulk structures or for low-moment expansions. I have shown how, in many cases, the BOP provides a good approximation to TB calculations. Even with just 9 moments in the expansion, the standard BOP method is able to reproduce the volume-dependence of the energies and magnetic moments of the major bulk structures of iron, as well as the transformations between those structures. The formation energy of, and relaxations surrounding, mono- and divacancies are also very similar in BOP and TB methods.

Nevertheless, the standard analytic BOP method has several deficiencies, notably the possibility of negative densities of states. While these have little effect on non-magnetic or bulk calculations, they can cause severe problems in achieving convergence of the energy in complex defects such as the self-interstitial atoms, or for non-collinear magnetic states. The negative DOS can be avoided, in some cases, by a judicious choice of  $a^{(\infty)}$  and  $b^{(\infty)}$ , although so far no consistently reliable *analytic* approximation has been found. The introduction of the damping factors of the Jackson kernel, borrowed from the Kernel Polynomial Method, however, do force the density of states to remain positive. The damping factors also smear out much of the structure of the DOS which must then be added back by the inclusion of additional, approximate moments. This hybrid method does indeed lead to a positive density of states and makes the calculation of defect structures more reliable, although the inclusion of hundreds of additional moments necessitates even better approximations for  $a^{(\infty)}$  and  $b^{(\infty)}$  to prevent the DOS from oscillating wildly.

The magnetic analytic BOP theory can be applied to any TB model whose DOS is continuous. For this reason, it is also applicable to non-collinear magnetic configurations. I have extended the formalism of the non-collinear magnetic analytic BOP to take into account the full matrix nature of the quantities required for calculations of the gradients, forces and torques necessary for future dynamic simulations. Test calculations on simple non-collinear structures, however, show that the binding energy is very sensitive to changes in the local magnetic moments, and even the small inaccuracies in the BOP moments can lead to a qualitatively incorrect behaviour of the energy. The rotational shape-dependence

of the TB local DOS also appears to involve high numbers of moments which are beyond the current reach of the BOPFOX implementation.

Throughout this work two things have become clear. One, is that more time needs to be spent developing accurate TB models for iron. In several cases poor BOP results, in comparison to DFT or experiment, were the result of an inadequate TB parametrisation (the BOP can never be better than the underlying TB model, after all). For example, the Madsen *et al.* model examined here predicts the incorrect magnetic states and energies for the SIA defects, as well as an unphysical expansion of the bcc (100) surface on relaxation. The non-collinear spin-dependence of the bond and exchange energies also seems questionable as does the non-collinear ground state for bcc Fe, a known inadequacy of *d*-only models. These artefacts of the model are reproduced by BOP. A better TB model might simply include more physical parameters in its fit database, such as the elastic constants or SIA defect formation energies. In other cases, the physical model must be extended to include *s* and *p* electrons (for accurate non-collinear calculations), orbital non-orthogonality, or a more complex model for charge transfer beyond the simple case of local charge neutrality.

The second realisation is that the BOP potential itself requires a dedicated parametrisation. Even with 20 moments, the analytic BOP is not able to reproduce the TB elastic shear constants. The SIA defect energies are consistently lower than TB, and the energy of non-collinear states (or even isolated antiferromagnetic moments) is very sensitive to the inaccuracies in the BOP magnetic moments. A separate BOP fitting for a given number of moments would be required to reproduce experimental or *ab initio* data in this case, as is already done for the numerical BOPs. Perhaps it was overly optimistic to think that all these physical properties could be reproduced by the BOP ‘out of the box’, without refitting the parameters. Nevertheless, the success of the numerical BOP method shows us that a 9-moment analytic BOP model is flexible enough to be parametrised for these particular problems, particularly with the positive DOS constraints of the extended BOP+ method.

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