Development of interatomic potentials in the
Tersoff-Albe formalism for metal compounds

Jesper Byggmästar
2016

Supervisors:  Morten Nagel
             Krister Henriksson
Examiners:   Krister Henriksson
             Kai Nordlund

UNIVERSITY OF HELSINKI
DEPARTMENT OF PHYSICS

PL 64 (Gustaf Hällströmin katu 2)
00014 Helsingin yliopisto
Interatomic potentials are used to describe the motion of the individual atoms in atomistic simulations. An accurate treatment of the interatomic forces in a system of atoms requires heavy quantum mechanical calculations, which are not computationally feasible in large-scale simulations. Interatomic potentials are computationally more efficient analytical functions used for calculating the potential energy of a system of atoms, allowing simulations of larger systems or longer time scales than in quantum mechanical simulations.

The interatomic potential functions must be fitted to known properties of the material the potential describes. Developing a potential for a specific material typically involves fitting a number of parameters included in the functional form, against a database of important material properties, such as cohesive, structural, and elastic properties of the relevant crystal structures. In the Tersoff-Albe formalism, the fitting is performed with a coordination-based approach, where structures in a wide range of coordination numbers are used in the fitting process. Including many differently coordinated structures in the fitting database is important to get good transferability to structures not considered in the fitting process.

In this thesis, we review different types of widely used interatomic potentials, and develop an iron-oxygen potential in the Tersoff-Albe formalism. We discuss the strengths and weaknesses of the developed potential, as well the challenges faced in the fitting process. The potential was showed to successfully predict the energetics of various oxygen-vacancy defect clusters in iron, and the basic properties of the common iron oxide wüstite. The potential might therefore mainly be applicable to atomistic simulations involving oxygen-based defects in solid iron, such as irradiation or diffusion simulations.
Interatomära potentialer används för att beskriva enskilda atomers rörelse i atomistiska simulerings- gär. En bra beskrivning av de krafter som verkar mellan enskilda atomer i ett system kräver tunga kvantmekaniska beräkningar, som begränsar antalet atomer som effektivt kan simuleras. Interatomära potentialer är numeriskt mera effektiva och simplare analytiska funktioner som ger potentielenergin för ett system av atomer. Beräkningsmässigt effektiva potentialer möjliggör simulerings av större system och längre tidsskalor än i kvantmekaniska simulerings.

Interatomära potentialer måste anpassas till egenskaperna av det material som potentialen beskriver. Utvecklingen av en potential innefattar typiskt en numerisk anpassning av ett antal parametrar som är inkluderade potentialfunktionen, med hjälp av en databas av viktiga materialegenskaper. Materialegenskaper som ofta tas i beaktande i anpassningen är kohesions-, struktur- och elastiska egenskaper hos de relevanta kristallstrukturerna. Grundidén i Tersoff-Albe-formalismen är en koordinationsbaserad anpassning, där egenskaperna hos strukturer med koordinationstal i ett brett intervall tas i beaktande. En koordinationsbaserad anpassning möjliggör att potentialen med stor sannolikhet också kan beskriva andra strukturer som inte inkluderats i anpassningen.

I denna avhandling diskuteras den fysikaliska bakgrunden hos olika typer av populära interatomära potentialer, samt utvecklingen av en järn-syre-potential i Tersoff-Albe-formalismen. Utmaningar i utvecklingen av potentialen, samt dess svagheter och styrkor diskuteras. Den anpassade järn-syre-potentialen visas kunna beskriva den relativa stabiliteten och energierna för en rad olika syre-vakansdefekter i järn, samt de viktigaste egenskaperna hos järnoxiden wüstit. Potentialens främsta tillämpningsområden är därför atomistiska simulerings där olika syrebaserade defekter i järn förekommer, såsom i jonbestrålingar av material eller diffusionssimuleringer.
Contents

1 Introduction 2

2 Interatomic potentials 4
   2.1 Overview of potential types 4
       2.1.1 Pair potentials 4
       2.1.2 Many-body potentials 6
       2.1.3 Molecular mechanics force fields 13
       2.1.4 Reactive force fields 14
   2.2 Tersoff-like potentials 16

3 Albe fitting formalism 24
   3.1 Formalism 24
   3.2 Examples 26
       3.2.1 Pt 26
       3.2.2 Fe 28
       3.2.3 O 29

4 Fitting of the Fe-O potential 33
   4.1 Data used in the fitting 33
   4.2 Fitting approach 37
   4.3 Results and discussion 40

5 Summary 50
1 Introduction

Theoretically predicting the motion of atoms in a system requires knowledge of the interactions between the individual atoms. Calculating interactions between individual atoms is a quantum mechanical task, but a pure quantum mechanical treatment of a system of many atoms is, however, virtually impossible to accomplish. Quantum mechanics-based simulation techniques, such as density functional theory, are also only viable for system sizes of the order of hundreds to thousands of atoms. Larger systems require simpler, numerically more efficient interaction models.

In large-scale atomistic simulations, such as molecular dynamics, the interactions between atoms are governed by a computationally efficient interatomic potential function, allowing simulations of much larger systems or longer time periods than possible in quantum mechanical simulations. An interatomic potential is typically a relatively simple analytical function used for calculating the total potential energy of a system of atoms, as a function of their individual and relative positions. In the earliest atomistic simulations in the mid-20th century, the atom trajectories were predicted by simple pair potentials, in which the potential energy is calculated as a sum of the bond energies of atom pairs [50]. However, pairwise calculated potential energy functions have severe limitations for predicting the behaviour and properties of crystalline materials [31]. Atomistic simulations could have aided the intensively studied new theories of dislocations and deformation of solid materials at the time, if not for the limitations of the pair potentials, together with poor computing power limiting the studies to very small systems. With limited computational resources, the efficient pair potentials still led to important results in physics and chemistry and solidified atomistic simulations as a powerful tool in materials physics and chemistry [50].

The continuously increasing computing power allowed simulations of larger and larger systems, but also development of more sophisticated and computationally more demanding potential functions. Guided by new theories of interatomic bonding, a set of different types of many-body potentials, such as the embedded atom method potentials and bond order potentials, were developed in the 1980s [18, 22, 54]. The many-body dependence of the potentials solved the shortcomings of the pair potentials and were still computationally efficient enough to be used in large-scale simulations. The improved accuracy and predictive capabilities of the potentials allowed for simulations of a large variety of processes in materials. With realistic treatment of bonds between atoms, i.e. bonds breaking and forming at accurate energies and bond lengths, many-body potentials could be, and are, today widely used in atom-
istic simulations of non-equilibrium processes, such as melting, dislocation movement, corrosion and effects of irradiation.

The two main requirements for a good interatomic potential function; computational efficiency, and the ability to predict a wide variety of material properties and phases, generally results in functions involving a number of parameters with no easily derived set values. An interatomic potential with its parameters must therefore be fitted according to a known set of physical properties. The most important properties usually included in the fitting process are the lattice parameters, cohesive or formation energies, bulk moduli, and elastic constants of the ground state and other important structures. Other properties considered when testing the potential might include for example the melting temperature, defect formation energies or surface energies. The values of the various properties used in the fitting process can be obtained from experimental studies, or density functional theory simulations. Fitting an interatomic potential to accurately predict all of the above-mentioned properties is no easy task, and often involves compromises. Typically, a poor description of less important properties have to accepted in favour of good descriptions of the properties prioritised in applications the potential is developed for. A good potential can still perform reasonably well for a wide array of structures and systems, and is transferable to systems not considered in the fitting process [12].

In this thesis, we review different types of commonly used interatomic potentials, and present a bond order potential for Fe-O interactions developed as a part of this work. The motivation and several parametrisations of the potential and their strengths and weaknesses are discussed.
2 Interatomic potentials

2.1 Overview of potential types

2.1.1 Pair potentials

Pair potentials are by far the simplest and oldest interatomic potentials used to describe a system of atoms. The interactions between the atoms in the system are generally incorporated in the potential function as an attractive and a repulsive part. The potential therefore has the form

$$U = U_{\text{rep.}} + U_{\text{attr.}}$$

(2.1)

where the second term is strictly negative, representing an attraction between the atoms. Figure 2.1 shows an example of the general shape of a potential, with the repulsive and attractive components plotted separately.

Figure 2.1: The repulsive and attractive parts of a pair potential as well as their sum, illustrating the shape of Equation 2.1.
The attractive part has its physical origin in the binding interactions between the atoms, be it metallic bonds, ionic bonds, covalent bonds, or any other bonds such as those due to weak van der Waals forces. Repulsive interactions between atoms become dominant at small interatomic separations. As the atoms move closer to each other, a combination of Coulombic forces between the electrons and the repulsion due to the Pauli exclusion principle will dominate over all attractive forces. The Pauli exclusion principle states that no two fermions (e.g. electrons) can occupy the same quantum state simultaneously. At even smaller separations, the Coulombic repulsion between the nuclei becomes the dominant effect.

Perhaps the most notable and widely used pair potential is the Lennard-Jones potential, dating back to 1924 and developed originally for weakly interacting gases, specifically argon [30]. In its most common form, the potential energy, \( U \), for two atoms at a distance \( r \) from each other is given by

\[
U(r) = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right]
\]  

(2.2)

where \( \varepsilon \) is the depth of the potential well and \( \sigma \) the distance at which the potential energy is zero. While the attractive interaction due to van der Waal forces indeed can be shown to be proportional to \(-r^{-6}\) as in Equation 2.2 above, the repulsive \( r^{12} \) behaviour has no physical motivation. It has simply proved to be a good enough choice while, more importantly, reducing the computational cost as the repulsive term can be computed as the attractive term squared. By choosing \( \varepsilon \) and \( \sigma \) to correspond to the experimentally obtained equilibrium separation and energy, the Lennard-Jones potential can fairly accurately describe any noble gas in near-equilibrium conditions (at low interatomic distances it fails badly due to the poorly motivated repulsive term).

Another well-known pair potential that is still important to this day is the Morse potential [35], published in 1929 as a good approximation for many (vibrating) diatomic molecules. It gives analytical solutions for the Schrödinger equation, and has the form

\[
U(r) = D e^{-2a(r-r_0)} - 2D e^{-a(r-r_0)}
\]

(2.3)

where \( D \) is depth of the potential well, \( r_0 \) the equilibrium bond distance, and \( a \) can be determined from the frequency of classical small vibrations, which in the Morse potential is given by:
\[ \omega_0 = \frac{a}{2\pi} \sqrt{\frac{2D}{\mu}} \]  

where \( \mu \) is the reduced mass. The Morse potential makes up the basis of many important many-body potentials, discussed in the next section.

Due to their simplicity, pair potentials have severe inherent limitations when used in atomistic simulations. The most crucial shortcoming for pair potentials, leading to a number of problems, is the complete lack of environmental dependence. The potential energy is evaluated purely as a function of the interatomic distance of single atom pairs, the geometry of the surrounding atoms are not taken into account in any way. Due to the lack of environmental consideration, e.g. surface effects and the vacancy formation energy in a solid are poorly described. In fact, it can be easily shown that the vacancy formation energy in a perfect crystal is equal to the cohesive energy with a pair potential, which is significantly higher than typical formation energies. The predicted ground state of a material described by a pure pair potential will always be a close-packed structure, i.e. the hexagonal close-packed (HCP) or the face-centred cubic (FCC) structure. This eliminates the possibility of accurately describing any e.g. body-centred cubic element with a pair potential. Furthermore, for a pairwise studied cubic system of atoms, the ratio of the elastic constants \( C_{12} \) and \( C_{44} \) will always be exactly equal to one, known as the Cauchy relation. This relation is violated in many elements, which a pair potential cannot predict. It is therefore of interest to develop and utilise more sophisticated potentials that address some, or all of the above-mentioned limitations.

### 2.1.2 Many-body potentials

In order to account for the surrounding atomic geometry of an atom in a system, the potential energy calculation must include additional many-body-dependent terms beyond the two-body term. In the most general form, the total potential energy of a system of \( N \) atoms can then be written

\[
U_{\text{tot}} = \sum_{i} U_1(r_i) + \sum_{i,j} U_2(r_i, r_j) + \sum_{i,j,k} U_3(r_i, r_j, r_k) + \ldots
\]  

(2.5)

where \( U_1, U_2, U_3 \) are the one-, two-, and three-body potentials and \( r_i \) the position vector of atom \( i \). The one-body term is only present if the system is subjected to an external field, such as an electric field. However, this is usually not the case, and the
potential energy is then independent of the actual positions of the atoms, and can be written in the slightly simpler general form using interatomic distances and angles:

\[ U_{\text{tot}} = \sum_{i,j}^N U_2(r_{ij}) + \sum_{i,j,k}^N U_3(r_{ij}, r_{ik}, \theta_{ijk}) + \ldots \]  

(2.6)

where \( r_{ij} \) is the distance between atoms \( i \) and \( j \), and \( \theta_{ijk} \) the angle between atoms \( i \), \( j \), and \( k \).

A number of different types of many-body potentials have been developed over the years, many originally introduced in the 1980s and since then further developed and applied to a broader set of materials. In this section, we will review some of the most widely used types of many-body potentials, starting with embedded atom method potentials developed mainly for metallic elements, the closely related Finnis-Sinclair potential, the Stillinger-Weber potential for Si, and finally we introduce the Tersoff potential (which, together with closely related potential forms, will be discussed in more detail in section 2.2).

The embedded atom method (EAM) formalism [18] is based on the principles of effective medium theory [41,52], in which an impurity in a metal can be seen as embedded in a cloud of electrons with a positive background (the nuclei), often called the jellium. The embedding energy is defined as the energy difference between an atom embedded in the jellium, and an atom separated from the jellium. It has been known for a long time that the energy can be expressed with a universal functional of the electron density [26], an important result that provides the basis for the widely used density functional theory. The embedding energy of the impurity can be determined by the charge of the impurity nucleus, and the electron density at the impurity position before it was embedded. The total energy of the host lattice with an impurity is therefore given as a universal functional (independent of host material) of the unperturbed host electron density

\[ U = \mathcal{F}_{Z,R}[\rho_h(r)] \]  

(2.7)

where \( Z \) and \( R \) are the atomic number and position of the impurity, and \( \rho_h(r) \) the electron density of the host without the impurity. The exact form of the functional is not known and is most likely too complicated for any practical use. As a local approximation, the energy of the impurity can be assumed to be a function of a uniform electron density of the local environment only. In an effective medium approach, the energy of the host lattice could be calculated with e.g. a pair potential, to which the
energy of the impurity is added to get the total energy. This method allows fairly accurate treatment of different impurities in metals, which as described in the previous section is often not possible in a pure pair potential treatment. The shortcomings of pair potentials related to the energy calculation of the lattice itself are, however, still not avoided. To address this, the EAM sees all atoms in the lattice as impurities, embedded in a host of all the other atoms. In the local approximation, the total energy can then be expressed as a sum of the embedding energies of each atom

\[ U = \sum_i F_i(\rho_{h,i}) \]  

(2.8)

where the embedding energy \( F_i \) is simply a function of the electron density at the position of atom \( i \), before atom \( i \) is embedded. It should be noted that the embedding function \( F \) is not trivially related to the functional \( \mathcal{F} \), as shown in [18].

The assumption of a uniform local electron density is generally not satisfied. In a real solid, the density is non-uniform. The needed corrections can be taken into account when determining the embedding function \( F \). Furthermore, Equation 2.8 does not take the repulsions between nuclei into account. The repulsion can be introduced as a simple pair potential between the nuclei. The total potential energy is then

\[ U = \sum_i F_i(\rho_{h,i}) + \frac{1}{2} \sum_{i \neq j} \phi_{ij}(r_{ij}) \]  

(2.9)

where \( r_{ij} \) is the distance between atoms \( i \) and \( j \). The electron density of the host at the position of atom \( i \), \( \rho_{h,i} \), can be approximated by

\[ \rho_{h,i} = \sum_{i \neq j} \rho_j(r_{ij}) \]  

(2.10)

where \( \rho_j(r_{ij}) \) is the contribution to the electron density at \( i \) by atom \( j \), and the total host electron density is a sum of the contributions of all atoms. The electron density of an atom can always be calculated using density functional techniques [45]. For the repulsive pair potential, a screened-charge potential in the form

\[ \phi_{ij}(r) = \frac{Z_i(r)Z_j(r)}{r} \]  

(2.11)

is generally used. Constructing an EAM potential practically means finding the functional form of the embedding energy \( F \) and the effective charge \( Z(r) \). The functions can be fitted to known experimental properties of the material, or properties obtained by density functional theory calculations.
The Finnis-Sinclair potential \cite{22} can be expressed in a form identical to the general EAM potential in Equation 2.9, with the embedding function \( F = A \sqrt{\rho_h} \) as

\[
U = A \sum_i \sqrt{\rho_{h,i}} + \frac{1}{2} \sum_{i \neq j} \phi_{ij}(r_{ij})
\]  
(2.12)

The square-root form of the embedding function is motivated by the second-moment approximation of the tight-binding model, which predicts that the electronic binding energy satisfies \( E_{el} \propto \sqrt{Z} \), where \( Z \) is the number of nearest neighbours.

Motivated by the lack of environmental dependence in pair potentials, another approach for developing more accurate many-body potentials is to focus on the local bonding configurations around an atom in the lattice. A strong dependence on the surrounding bonding geometry is particularly important to correctly reproduce the structures of covalently bonded materials. The Stillinger-Weber potential, developed for Si \cite{51}, includes an explicit angular dependence to correctly minimise the energy for the ground state diamond structure. The potential energy is given by

\[
U = \sum_{i<j} \varepsilon f_2(r_{ij}/\sigma) + \sum_{i<j<k} \varepsilon f_3(r_i/\sigma, r_j/\sigma, r_k/\sigma)
\]  
(2.13)

where \( \varepsilon \) and \( \sigma \) are energy and length unit parameters. The pair potential \( f_2 \) has the form

\[
f_2(r) = \begin{cases} 
A(Br^{-p} - r^{-q}) \exp[(r-a)^{-1}] & , r < a \\
0 & , r \geq a 
\end{cases}
\]  
(2.14)

where \( A, B, p, \) and \( q \) are positive parameters. A cutoff is applied at \( r = a \), for computational efficiency. The three-body function is given by

\[
f_3(r_i/\sigma, r_j/\sigma, r_k/\sigma) = h(r_{ij}, r_{ik}, \theta_{jik}) + h(r_{ji}, r_{jk}, \theta_{ijk}) + h(r_{ki}, r_{kj}, \theta_{ikj})
\]  
(2.15)

where \( \theta_{jik} \) is the angle between the vectors \( r_{ij} \) and \( r_{ik} \). The function \( h \) is given by

\[
h(r_{ij}, r_{ik}, \theta_{jik}) = \begin{cases} 
\lambda \exp[\gamma(r_{ij} - a)^{-1}] + \gamma(r_{ik} - a)^{-1}] (\cos \theta_{jik} + \frac{1}{3})^2 & , r_{ij}, r_{ik} < a \\
0 & , r_{ij} \text{ or } r_{ik} \geq a 
\end{cases}
\]  
(2.16)

where \( \lambda \) and \( \gamma \) are positive parameters. The function explicitly favours tetrahedral
bonds in the diamond lattice, where \( \cos \theta = -\frac{1}{3} \). The different parameters were fitted to get the diamond structure as the ground state and to get an accurate melting temperature. The explicit angular dependence, while resulting in good behaviour for the diamond structure, has the drawback of not describing any other structure very well. Consequently, the potential formalism cannot be widely transferred to other elements with other ground state structures. A more transferable formalism can be obtained by including a bond order dependence (i.e. the strength of each bond) while still retaining an angular term. An explicit dependence on the local bond order provides the basis for the Tersoff-like potentials.

By keeping the principle of bond order as the basis of the formalism, Tersoff [54] assumed an interatomic potential in the form

\[
U = \frac{1}{2} \sum_{i \neq j} f_C(r_{ij})[a_{ij}f_R(r_{ij}) + b_{ij}f_A(r_{ij})] \tag{2.17}
\]

where \( f_R \) and \( f_A \) are repulsive and attractive pair potentials, and \( f_C \) a smooth cutoff function. Morse potentials proved to be good choices for the basis pair potentials, given by

\[
f_R(r) = Ae^{-\lambda_1 r} \tag{2.18}
\]
\[
f_A(r) = -Be^{-\lambda_2 r} \tag{2.19}
\]

The cutoff function was chosen as a smooth, continuous, and differentiable function with values between 0 and 1. It has the form

\[
f_C(r) = \begin{cases} 
1 & , r < R - D \\
\frac{1}{2} - \frac{1}{2} \sin \left( \frac{\pi}{2} (r - R) / D \right) & , R - D < r < R + D \\
0 & , r > R + D 
\end{cases} \tag{2.20}
\]

The function \( b_{ij} \) is the essential part of the potential and represents a measure of the bond order. It is a monotonically decreasing function of the coordination numbers of atoms \( i \) and \( j \), and takes the form

\[
b_{ij} = (1 + \beta^n \zeta_{ij}^n)^{-1/2n} \tag{2.21}
\]

where

\[
\zeta_{ij} = \sum_{k \neq i, j} f_C(r_{ik})g(\theta_{ijk})e^{\lambda_3 (r_{ij} - r_{ik})^3} \tag{2.22}
\]
\[ g(\theta) = 1 + \frac{c^2}{d^2} - \frac{c^2}{d^2 + (h - \cos \theta)^2} \] (2.23)

\( \theta_{ijk} \) is the angle between the bonds \( ij \) and \( ik \). The function \( a_{ij} \) serves the purpose of limiting the range of the repulsive interactions, and was chosen to have the form

\[ a_{ij} = (1 + \alpha^m \eta_{ij}^n)^{-1/2n} \] (2.24)

with

\[ \eta_{ij} = \sum_{k \neq i,j} f_{C}(r_{ik}) e^{-\lambda_3 (r_{ij} - r_{ik})^3} \] (2.25)

However, \( a_{ij} \) is generally not used (by setting \( \alpha = 0 \Rightarrow a_{ij} = 1 \)), but was included for completeness. The remaining set of unmentioned terms are parameters to be empirically fitted against a database of material properties. The Tersoff potential is essentially nothing but a pair potential, but with an implicit three-body dependence through the bond order function, making it computationally efficient for use in large-scale atomistic simulations. The physical motivation behind the Tersoff potential, as well as similar alternative representations of the potential form, will be discussed in more detail in section 2.2.

At this point, it is interesting to note that despite the seemingly very different physical approach, the EAM potential can be expressed in a form equivalent to the Tersoff formalism, as shown by Brenner [9] and recited below. The attractive part of the Tersoff potential, with the implicit many-body dependence for an atom \( i \) is given as presented above by

\[ U_i^A = \frac{1}{2} \sum_{j(\neq i)} b_{ij} B e^{\lambda_3 r_{ij}} \] (2.26)

with

\[ b_{ij} = \left[ 1 + \beta^n \left( \sum_{k \neq i,j} f_{C}(r_{ik}) g(\theta_{ijk}) e^{-\lambda_3 (r_{ij} - r_{ik})^3} \right)^n \right]^{-1/2n} \] (2.27)

Recall that the corresponding attractive many-body part of the EAM potential for an atom \( i \) is given by

\[ U_i^A = F(\rho_{h,i}) = F \left( \sum_{j(\neq i)} \rho_j(r_{ij}) \right) \] (2.28)

Assuming the Finnis-Sinclair form for the embedding function, \( F_i = A \sqrt{\rho_h} \), and the (physically well-motivated) exponential approximation for the atomic electron density,
we have

\[ U^A_i = A \left( \sum_{j(\neq i)} e^{-ar_{ij}} \right)^{1/2} \]  

(2.29)

Following a few algebraic steps, Equation 2.29 can be manipulated into a form similar to the Tersoff term in Equation 2.26:

\[ U^A_i = A \left( \sum_{j(\neq i)} e^{-ar_{ij}} \right)^{1/2} = A \left( \sum_{j(\neq i)} e^{-ar_{ij}} \right) \left( \sum_{k(\neq i)} e^{-ar_{ik}} \right)^{-1/2} \]  

(2.30a)

\[ = A \sum_{j(\neq i)} \left[ e^{-ar_{ij}} \left( \sum_{k(\neq i)} e^{-ar_{ik}} \right)^{-1/2} \right] \]  

(2.30b)

\[ = A \sum_{j(\neq i)} \left[ e^{-ar_{ij}} \left( e^{-ar_{ij}} + \sum_{k(\neq i, j)} e^{-ar_{ik}} \right)^{-1/2} \right] \]  

(2.30c)

\[ = A \sum_{j(\neq i)} \left[ e^{-ar_{ij}} \left( e^{-ar_{ij}} + e^{-ar_{ij}} \sum_{k(\neq i, j)} e^{a(r_{ij} - r_{ik})} \right)^{-1/2} \right] \]  

(2.30d)

\[ = \sum_{j(\neq i)} A e^{-ar_{ij}/2} \left( 1 + \sum_{k(\neq i, j)} e^{a(r_{ij} - r_{ik})} \right)^{-1/2} \]  

(2.30e)

By choosing \( A = B/2 \) and \( a = 2\lambda_2 = \lambda_3 \), we get Equation 2.26 with the bond order function

\[ b_{ij} = \left( 1 + \sum_{k(\neq i, j)} e^{\lambda_3(r_{ij} - r_{ik})} \right)^{-1/2} \]  

(2.31)

which with \( n = \beta = g(\theta) = 1 \) is very similar to the Tersoff bond order function in Equation 2.27 (apart from the powers of three in the exponential term), and identical to the similar bond order form used by Brenner [8]. The only noteworthy difference between the formalisms, due to the choice of parameters to prove the equivalence, is the loss of explicit angular dependence when requiring \( g(\theta) = 1 \).

Although the EAM potential was originally developed for metals, and the Tersoff potential for covalently bonded semiconductors, the above derived close relationship shows that there is nothing preventing the Tersoff formalism from being fitted to metallic elements. As will be discussed in later sections, Tersoff-like potentials have indeed been applied to a wide range of materials, including metals and metallic carbide and oxide compounds.
2.1.3 Molecular mechanics force fields

Describing molecules requires that the potential energy has a strong dependence on the geometry of the molecule, and deviations from the equilibrium geometry. Potential energy functions designed for molecules might therefore include terms not necessary in the many-body potentials discussed in the previous section. The total energy of a molecule in a molecular mechanics force field involves at least bonding terms for intramolecular interactions, an angular dependence, and a rotational dependence. In its most general form, the energy of a molecule can be written

\[ U = U_{\text{bond}} + U_{\text{angle}} + U_{\text{torsion}} + U_{\text{out-of-plane}} + U_{\text{cross}} + U_{\text{non-bond}} \]  

(2.32)

The bond term corresponds to the chemical bonds within the molecule. It is usually taken as a harmonic pair potential in the form of Hooke’s law:

\[ U_{\text{bond}}(r) = \sum_{\text{bonds}} \frac{1}{2} k (r - r_0)^2 \]  

(2.33)

where \( k \) is a well-chosen parameter and \( r_0 \) the reference bond length. The harmonic potential describes bonds that are resistant to bond stretching. More importantly, due to the symmetry of Equation 2.33, it is immediately apparent that bonds are not able to break. Stretching the bond further and further will result in a continuous increase of the opposing force. Molecular mechanics force fields are therefore limited to non-reacting molecules. To give a more realistic approximation of bonds far from equilibrium, it is possible to include higher order terms in Equation 2.33 or replace it with a Morse potential.

Similarly, the angular term is often given in the form

\[ U_{\text{angle}}(\theta) = \sum_{\text{angles}} \frac{1}{2} h (\theta - \theta_0)^2 \]  

(2.34)

where again, higher order terms can be included for improved accuracy. The angular function guarantees that the intramolecular angles remain close to the equilibrium angle \( \theta_0 \).

For many molecules, possible rotation or torsion of the bond must be taken into account. Due to the symmetry and periodicity of the rotation, it is clear that the rotational term is best expressed with a trigonometric function. A common choice is a cosine series of \( N \) terms in the form, or similar to
\[ U_{\text{torsion}}(\phi) = \sum_{n=0}^{N} C_n \cos(\phi)^n \]  

(2.35)

where \( \phi \) is the torsion angle and \( C_n \) constants.

In some molecules, such as a benzene ring, the atoms are known to stay in the same plane. favouring a planar molecule can be done by including an "out-of-plane" function in any appropriate form. A simple choice is again a harmonic function

\[ U_{\text{out-of-plane}}(d) = \sum_{i} \frac{1}{2} d_i^2 \]  

(2.36)

where \( d \) can be either the displacement from the preferred plane, or the corresponding angle.

The cross term \( U_{\text{cross}} \) includes any combinations of the above-mentioned interactions. For example, in some molecules, a decrease in the bond angle between atoms can be coupled with a stretch of the bond lengths to account for the atoms otherwise getting closer to each other. In the most general case, cross terms between all the above interactions would be included in the total energy calculation, but it is often found that only a few are necessary.

Finally, the non-bond term includes other interactions between the atoms and molecules present in the system, namely electrostatic and van der Waals forces. The electrostatic forces can be described by a Coulomb-like potential, where the charges typically are partial charges. The van der Waals interactions are well described by the Lennard-Jones potential.

Once a complete functional form of the total energy is chosen, the various parameters present in the included functions are fitted to a set of known properties of the target molecules. A good force field is transferable to a large number of molecules.

2.1.4 Reactive force fields

The fundamental shortcoming of ordinary force fields described in the previous section, that bonds are not able to break, sets a demand for a more sophisticated potential model for describing chemical reactivity of molecules. van Duin et al. [55] developed a reactive force field (ReaxFF), with a form similar to the non-reactive force field, but where the harmonic potentials are abandoned to allow bonds breaking and forming. The original force field was developed for hydrocarbons, but has since been parametrised and used for a number of other elements and compounds [14,15,40,42].
The total energy is split into the following terms:

\[ U = U_{\text{bond}} + U_{\text{over}} + U_{\text{under}} + U_{\text{val}} + U_{\text{pen}} + U_{\text{tors}} + U_{\text{conj}} + U_{\text{vdWaals}} + U_{\text{Coulomb}} \] (2.37)

\( U_{\text{bond}} \) is the bond energy term, approximated by an exponential function of the bond order. The bond order itself is a sum of exponential terms for \( \sigma \)- and \( \pi \)-bonds (multiplied by a set of correction factors). The bond energy term is the crucial difference between ReaxFF and ordinary force fields, allowing bond breaking.

The \( U_{\text{over}} \) and \( U_{\text{under}} \) terms are functions for restricting the coordination of an atom. For an overcoordinated atom, \( U_{\text{over}} \) imposes an energy penalty on the total energy, and similarly for an undercoordinated atom and \( U_{\text{under}} \). \( U_{\text{val}} \) is an angular function, parametrised to favour the angles present in different structures and molecules. \( U_{\text{pen}} \) is an additional penalty function for stabilising certain hydrocarbon systems with two double bonds. Bond torsions are taken into account with the function \( U_{\text{tors}} \), in a way similar to that described in the previous section. The effects of conjugated bonds are accounted for with the function \( U_{\text{conj}} \). \( U_{\text{vdWaals}} \) is a Morse-like potential describing the van der Waals interaction. The ionic interactions due to charges are taken into account with a shielded Coulomb potential as \( U_{\text{Coulomb}} \). Both the van der Waals and Coulombic interactions are calculated for all atom pairs in the system.

Some of the terms in the original expression for the total energy described above might not always be needed when parametrising a ReaxFF potential. While the bond energy term, the angular term, and the long-range Coulombic and van der Waals terms are vital for correctly stabilising the molecules and structures, the various functions restricting and penalising wrong coordination, torsion, or conjugation might not always be important. For instance, in the parametrisation for zinc oxides [46], only the bond, the overcoordination, the angular, and the van der Waals and Coulombic terms were included and the rest set equal to zero.
2.2 Tersoff-like potentials

The Tersoff and Tersoff-like potentials have been very successful in describing a wide range of materials, from covalently bonded elements to pure metals and metal compounds. In this section, we will revisit the Tersoff potential to discuss the physical motivation behind the functional form, as well as introduce other, slightly modified versions of the potential.

Recall the form of the Tersoff potential given in Equation 2.17

\[
U = \frac{1}{2} \sum_{i \neq j} f_C(r_{ij})\left[f_R(r_{ij}) + b_{ij}f_A(r_{ij})\right]
\] (2.38)

where we already set \(a_{ij} = 1\), as is practically always the choice. The choice of potential was largely motivated by the work of Abell [2], who showed that Morse-like potentials for the repulsive and attractive functions are in general good choices. It was therefore reasonable to choose

\[
f_R(r) = Ae^{-\lambda_1 r}
\] (2.39)

\[
f_A(r) = -Be^{-\lambda_2 r}
\] (2.40)

which with \(\lambda_1 = 2\lambda_2\) is identical to the Morse potential given earlier in Equation 2.3.

Tersoff chose not to incorporate many-body effects in explicit many-body terms, but to use a pair potential basis where all many-body dependencies enter through the bond order function \(b_{ij}\). A physically well-motivated description of the bond order is therefore essential to the success of the potential. It is well understood that an atom with many neighbours forms weaker individual bonds than an atom with very few neighbours. It is clear that the bond order should therefore be dependent on the coordination \(Z\). Abell showed that this dependence should be \(b_{ij} \propto Z^{-\delta}\), where \(\delta > 0\). Specifically, in the second order approximation of the tight binding model (previously mentioned as the motivation for the EAM-like Finnis-Sinclair potential), \(b_{ij} \propto Z^{-1/2}\).

Consider the Tersoff potential in Equation 2.38. Assuming only nearest neighbours are included, the cohesive energy for an atom \(i\) is then

\[
U_i(r_0) = E_{coh} = \frac{Z}{2} (Ae^{-\lambda_1 r_0} - b_{ij}Be^{-\lambda_2 r_0})
\] (2.41)

The equilibrium nearest neighbour distance \(r_0\) is obtained when \(\frac{dU_i(r)}{dr} \bigg|_{r=r_0} = 0\), from
which we get

\[
\frac{Z}{2} \left( -\lambda_1 A e^{-\lambda_1 r_0} + \lambda_2 b_{ij} B e^{-\lambda_2 r_0} \right) = 0 \quad (2.42a)
\]

\[
\lambda_2 b_{ij} B e^{-\lambda_2 r_0} = \lambda_1 A e^{-\lambda_1 r_0} \quad (2.42b)
\]

Substituting (2.42) into (2.41) gives the cohesive energy

\[
E_{\text{coh}} = \frac{Z}{2} b_{ij} B \left( \frac{\lambda_2}{\lambda_1} - 1 \right) e^{-\lambda_2 r_0} \quad (2.43)
\]

or equivalently

\[
E_{\text{coh}} = \frac{Z}{2} A \left( 1 - \frac{\lambda_1}{\lambda_2} \right) e^{-\lambda_1 r_0} \quad (2.44)
\]

Two important observations can be made from these equations. By choosing \( \lambda_1 = 2 \lambda_2 \) as in a pure Morse potential, the energy per bond can, using e.g. (2.44) simply be written

\[
E_{\text{bond}} = -A e^{-2\lambda_2 r_b} \quad (2.45)
\]

which is equivalent to the empirical Pauling relationship between bond energy and bond length \( (r_b) \) \[43\], supporting the choice of Morse-like potentials to correctly describe bond strengths. Secondly, at higher coordinations, the cohesive energy for many elements show a relatively weak dependence on the coordination. By choosing a bond order function as the previously motivated \( b_{ij} \propto Z^{-1/2} \) and keeping \( \lambda_1 = 2 \lambda_2 \), we get from equation (2.42)

\[
e^{-\lambda_2 r_0} = \frac{b_{ij} B}{2A} \propto \frac{B}{2A\sqrt{Z}} \quad (2.46)
\]

and substituting into (2.41) gives

\[
E_{\text{coh}} = \frac{Z}{2} \left[ A \left( \frac{B}{2A\sqrt{Z}} \right)^2 - \frac{B}{\sqrt{Z}} \frac{B}{2A\sqrt{Z}} \right] = -\frac{B^2}{8A} \quad (2.47)
\]

i.e. with \( b_{ij} \propto Z^{-1/2} \), the cohesive energy is independent of coordination, supporting the earlier mentioned weak dependence for higher coordinations in e.g. Si \[54\]. Surely, the cohesive energy cannot be completely independent of coordination, but it is reasonable to assume that \( b_{ij} \propto Z^{-\delta} \) with \( \delta \approx 1/2 \) at coordinations close to each other in energy, with a minimum at the ground state coordination.

Due to the bond order function being the only many-body dependent factor in the Tersoff potential, the importance of angular dependence in covalently bonded struc-
tures also requires $b_{ij}$ to be a function of angles between bonds. Furthermore, bond distances must be included in $b_{ij}$, to prevent all structures with the same coordination having exactly the same energy. By keeping the coordination dependence as the main focus, Tersoff chose a bond order function in the form

$$b_{ij} = (1 + \beta^n \zeta_{ij}^n)^{-1/2n}$$

(2.48)

where $\beta$ and $n$ are parameters and $\zeta$ essentially counts the surrounding neighbours to get an effective coordination. The angular and bond length dependencies are embedded in $\zeta$ according to

$$\zeta_{ij} = \sum_{k \neq i,j} f_C(r_{ik}) g(\theta_{ijk}) e^{\lambda_3 (r_{ij} - r_{ik})^3}$$

(2.49)

with

$$g(\theta) = 1 + \frac{c^2}{d^2} - \frac{c^2}{d^2 + (h - \cos \theta)^2}$$

(2.50)

The parameters in the bond order function allows for tweaking the coordination, angular, and bond length dependence to accurately describe a given material. The $h$ parameter should be chosen carefully to be close the cosine of optimal angle in the ground state structure. However, naively setting $h$ to favour the optimal angle may result in a poor description of the elastic constants, since the forces counteracting deviations from the equilibrium bond lengths and angles might become unphysically large. The $c$ parameter can be tweaked to determine the strength of the angular dependence, and $d$ how sharp the angular dependence is.

Figure 2.2 illustrates the effect of the bond order function value in a Tersoff potential. At very low coordinations, such as a simple dimer, the bond order value is close to 1 and the strength of the single bond is relatively strong. For higher coordinations, the lower bond order values correctly shifts the potential curve to higher equilibrium distances and weaker bond strengths. Knowing the correct equilibrium distance, and assuming only nearest neighbours are within the cutoff range, it is possible to determine the value of the bond order function needed in order to shift the potential minimum to the corresponding reference minimum. Naturally, in the limit of the bond order approaching zero, the potential is purely repulsive.

Despite the well-motivated transferability of the Tersoff potential due to the coordination and angular dependent bond order function, it has some shortcomings that can prove to be severely affecting the physical accuracy in some materials. For example, long-range interactions such as electrostatic and the non-bonding van der
Waals interactions are not explicitly incorporated into the potential form. The lack of charge dependence can be problematic in highly ionic compounds. The Morse-like repulsive potential also leads to unphysical description of atoms very close to each other. The repulsive effects are important in simulations far from equilibrium, such as irradiation damage in materials where high movements are involved and accurate short-range repulsions between atoms are critical. A widely used, simple correction for the repulsive part will be discussed later in this section.

The pure Tersoff form is also inadequate for describing the chemical bonding nature in some molecules. In order to use the Tersoff formalism for describing hydrocarbons, Brenner modified the potential form to account for the bonding nature of certain hydrocarbon molecules [10]. The appearance and behaviour of conjugated bonds in molecules are often poorly described by a pure Tersoff potential. By restricting the interactions to nearest neighbours, atoms with single bonds can have an identical environment to atoms with conjugated bonds, so the distinction between bond types cannot be made in the Tersoff form. Similarly, bonds between atoms with different

![Figure 2.2: The effect of the bond order function on a Tersoff potential.](image)
coordinations might lead to problems. For instance, a vacancy in diamond will result in four radicals, i.e. the four atoms surrounding the vacancy will have normal, single bonds between their (now three) neighbours, and unpaired valence electrons due to the missing bond. The bond order dependence in a Tersoff potential will, however, result in an unphysical strengthening of the remaining bonds of the neighbouring atoms of the vacancy, due to the different coordinations. To achieve a better description of the chemical bonding in hydrocarbon molecules and structures, Brenner utilised the Tersoff form with added corrections in the bond order function. The potential was written in the similar general form

\[ U = \sum_i \sum_{j(i > i)} f_C(r_{ij}) [V_R(r_{ij}) - \bar{b}_{ij} V_A] \]  

(2.51)

where \( f_C \) is the cutoff function. The repulsive and attractive potentials are rewritten to make the correspondence to the Morse potential more apparent

\[ V_R(r_{ij}) = \frac{D}{S-1} e^{-\beta \sqrt{2S}(r_{ij} - r_0)} \]  

(2.52)

\[ V_A(r_{ij}) = \frac{SD}{S-1} e^{-\beta \sqrt{2/2S}(r_{ij} - r_0)} \]  

(2.53)

\( D \) is the potential well depth for the \( ij \) interaction and \( r_0 \) the equilibrium distance. If \( S = 2 \), \( V_R - V_A \) reduces to the Morse potential. The bond order function is written

\[ \bar{b}_{ij} = \frac{b_{ij} + b_{ji}}{2} + F_{ij}(N_i, N_j, N_{ij}^{\text{conj}}) \]  

(2.54)

to make \( \bar{b}_{ij} \) symmetric (as opposed to \( b_{ij} \)). \( F_{ij} \) is a correction function of the total number of neighbours \( N_i, N_j \) of atom \( i \) and \( j \), and whether the bond \( ij \) is conjugated, given by \( N_{ij}^{\text{conj}} \). Another correction function, \( H_{ij} \), is added to \( b_{ij} \):

\[ b_{ij} = \left[ 1 + \sum_{k(i \neq i,j)} f_C(r_{ij}) g(\theta_{ijk}) e^{\alpha_{ijk} [(r_{ij} - r_{0,ij}) - (r_{kj} - r_{0,kj})]} + H_{ij}(N^H_i, N^C_i) \right]^{-\delta} \]  

(2.55)

\( N^H_i \) and \( N^C_i \) are (specifically for the hydrocarbon potential) the number of H and C atoms bonded to atom \( i \). \( g(\theta_{ijk}) \) is given similarly to the Tersoff form as

\[ g(\theta) = a_0 \left[ 1 + \frac{c^2}{d} - \frac{c^2}{d^2 + (1 + \cos \theta)^2} \right] \]  

(2.56)

Whether a bond is part of a conjugated system can be determined by looking at the
number of neighbours of neighbouring atoms. For example, if a carbon has another carbon atom neighbour with a coordination less than four, the bond will be conjugated. If the coordination of the neighbouring carbon atom is exactly four, the bond is a normal single bond. The value of $N_{ij}^{\text{conj}}$ for a bond between carbon atoms $i$ and $j$ is given by

$$N_{ij}^{\text{conj}} = 1 + \sum_{k(\neq i,j)} f_C(r_{ik})P(x_{ik}) + \sum_{l(\neq i,j)} f_C(r_{jl})P(x_{jl})$$

(2.57)

where the sums go over carbon atoms only. $P(x_{ik})$ is a continuous function given by

$$P(x_{ik}) = \begin{cases} 
1 & x_{ik} \leq 2 \\
\frac{1}{2} + \frac{1}{2} \cos[\pi(x_{ik} - 2)] & 2 < x_{ik} < 3 \\
0 & x_{ik} \geq 3
\end{cases}$$

(2.58)

and $x_{ik} = N_k - f_C(r_{ik})$, where $N_k$ is the number of neighbours of atom $k$. Equation 2.57 gives continuous values for any neighbour geometries, also when bonds are breaking and forming. If $N_{ij}^{\text{conj}} = 1$, the bond is not conjugated, if $N_{ij}^{\text{conj}} \geq 2$, the bond is conjugated. The correction functions $H_{ij}$ and $F_{ij}$ in Equations 2.54 and 2.55, taking $N_{ij}^{\text{conj}}$ and the specific atom neighbourhood into account, are cubic splines interpolated between values for discrete numbers of neighbours. Following the success of the potential, Brenner et al. later developed an improved version, a second-generation reactive empirical bond order potential (REBO) [11], based on the original form presented above. Changes in the analytical form as well as the parameters being fit to a broader set of target properties, resulted in an overall better description of carbon and hydrocarbon structures and molecules.

As a final functional form in the Tersoff family of potentials, we present what we from now on refer to as the analytical bond order potential (ABOP), which is essentially the Brenner potential without the added correction functions. The total potential energy in the ABOP form is again written

$$U = \sum_i \sum_{j(\neq i)} f_C(r_{ij})[V_R(r_{ij}) - \overline{b}_{ij}V_A]$$

(2.59)

where the repulsive and attractive functions takes the same form as in the Brenner
potential

\[ V_R(r_{ij}) = \frac{D_0}{S-1} e^{-\beta\sqrt{2S}(r_{ij} - r_0)} \]  

(2.60)

\[ V_A(r_{ij}) = \frac{SD_0}{S-1} e^{-\beta\sqrt{2/S}(r_{ij} - r_0)} \]  

(2.61)

and the cutoff function is given by

\[
f_C(r) = \begin{cases} 
1 & , r \leq R - D \\
\frac{1}{2} - \frac{1}{2} \sin \left( \frac{\pi}{2} (r - R)/D \right) & , R - D < r < R + D \\
0 & , r \geq R + D 
\end{cases} \]  

(2.62)

The bond order function is written in the symmetric form

\[ \overline{b}_{ij} = \frac{b_{ij} - b_{ji}}{2} \]  

(2.63)

where

\[ b_{ij} = (1 + \chi_{ij})^{-p} \]  

(2.64)

The parameter \( p \) is generally fixed to \( 1/2 \), to get the square-root dependence of the bond order, but can also be taken as a fitting parameter if needed. Furthermore, \( \chi_{ij} \) is given by

\[ \chi_{ij} = \sum_{k(\neq i,j)} f_C(r_{ik}) g_{ik} (\theta_{ijk}) \omega_{ijk} e^{\alpha_{ijk}(r_{ij} - r_{ik})} \]  

(2.65)

and the angular function similar to the Tersoff and Brenner forms by

\[ g(\theta) = \gamma \left[ 1 + \frac{c^2}{d^2} - \frac{c^2}{d^2 + (h + \cos \theta)^2} \right] \]  

(2.66)

The \( \alpha_{ijk} \) parameter is in some versions replaced by the two-body parameter \( 2\mu \), which is in many cases set to zero. The three-body \( \omega_{ijk} \) parameter in Equation 2.65 is new compared to the Tersoff and Brenner potentials. If \( \omega_{ijk} = 1 \) for all \( ijk \) triplets, the bond order function reduces to a form similar to the Tersoff form. If, on the other hand, \( \omega_{ijk} = e^{-\alpha_{ijk}(r_{ij} - r_{0,ijk})} \), the bond order function is identical to the Brenner version in Equation 2.55. Keeping \( \omega_{ijk} \) as separate parameters allows one to choose values according to any of the above-mentioned options, or as free individual parameters to be fitted to the target properties of particularly problematic compounds.

In case of high energy events, such as simulations of collision cascades due to high-energy ion irradiation, the repulsive potential can be modified to give a more accu-
rate behaviour at interatomic distances much shorter than in typical near-equilibrium simulations. Another repulsive function, $V_{R'}(r)$, in addition to the original Morse-like $V_R^{\text{orig}}(r)$, is often included as

$$V_R^{\text{mod}}(r) = [1 - F(r)]V_{R'}(r) + F(r)V_R^{\text{orig}}(r)$$  \hspace{1cm} (2.67)

where $F(r)$ is the Fermi function

$$F(r) = \frac{1}{1 + e^{-b_f(r-r_f)}}$$  \hspace{1cm} (2.68)

$b_f$ and $r_f$ are chosen so that the near-equilibrium properties are nearly unchanged for all relevant coordinations, and a smooth fit to the short-range repulsive potential is achieved. The Fermi function gives values smoothly between 0 and 1, and its use has no physical motivation. A common choice for the added repulsive potential $V_{R'}$ is the Ziegler-Biersack-Littmark universal repulsive potential [59].
3 Albe fitting formalism

3.1 Formalism

Fitting the parameters of Tersoff-like interatomic potentials can be done in a systematic way as outlined by Albe et al. \[3\]. For an interatomic potential in the ABOP form, the parameters of the Morse potential terms can be determined based on experimental or theoretical (density functional theory) calculations. The parameter $D_0$ is directly given by the dimer bond energy, and $r_0$ by the dimer bond distance. The $\beta$ parameter can be determined using the ground state frequency of the dimer molecule, similar to the Morse potential in Equation 2.4 with $a = \beta$ and $\omega_0 = ck$, where $c$ is the speed of light and $k$ the wave number corresponding to the ground state frequency $\omega_0$, as

$$\beta = k \frac{2\pi c}{\sqrt{2} D_0 / \mu}$$

(3.1)

where $\mu$ the reduced mass of the dimer.

The remaining parameter of the Morse-like potential $S$ can be estimated by a coordination-based approach using the Pauling relation. Following the same procedure as for the Tersoff potential in the previous section, the energy per bond for an atomic system with only nearest neighbours included can be calculated as follows. In the ABOP form, the cohesive energy per atom is then given by

$$E_{coh} = \frac{Z}{2} \left[ V_R(r_b) - \bar{b}_{ij} V_A(r_b) \right] = \frac{Z}{2} \left[ \frac{D_0}{S - 1} e^{-\beta \sqrt{2S(r-r_b)}} - \bar{b}_{ij} \frac{SD_0}{S - 1} e^{-\beta \sqrt{2S(r-r_b)}} \right]$$

(3.2)

where $r_b$ is the bond distance to the nearest neighbours, and $\bar{b}_{ij}$ is assumed to have the appropriate value for correctly reproducing the cohesive energy at $r_b$. From the condition that the potential has a minimum at $r_b$, $\frac{dV_{ij}(r)}{dr} \bigg|_{r=r_b} = 0$, we get (after a few algebraic steps)

$$\bar{b}_{ij} e^{-\beta \sqrt{2S(r-r_b)}} = e^{-\beta \sqrt{2S(r-r_b)}}$$

(3.3)

By combining the above equations, we can write the energy per bond, or the Pauling relation between bond energy and bond length, as

$$E_{bond} = \frac{E_{coh}}{Z/2} = D_0 e^{-\beta \sqrt{2S(r-r_b)}}$$

(3.4)

Knowing the lattice parameters and cohesive energies of multiple structures with different coordinations, the parameter $S$ can be chosen so that the Pauling relation is
satisfied for all relevant coordinations. The agreement with the Pauling relation can be illustrated by a so-called Pauling plot, a semi-logarithmic plot of the bond energy as a function of the bond distance (see Figure 3.1). The $S$ parameter determines the slope of the curve in the Pauling plot. A good coordination-based fit is crucial in order for the potential to be transferable to structures and systems not considered in the fitting process.

The effective strength of the bond order can in principle be determined based on the Pauling analysis. Assuming the Pauling relation is satisfied for all reference structures, the value of the bond order function for each coordination should shift the potential depth and minimum to the corresponding cohesive energy and nearest neighbour distance of the reference structure. Finding values for the individual parameters of the bond order function corresponding to the correct bond lengths and cohesive energies for the different coordinations, is typically most efficiently done by numerical optimisation. The fitting database generally consists of at least cohesive energies, lattice parameters, and bulk moduli for different structures with different coordinations. Other properties, such as the elastic constants, pressure derivative of the bulk modulus, and formation energies for important defects are also often included, if available. Naturally, the numerical fit is guided to give the most accurate description for the ground state structure, and other energetically stable structures that are of interest. It should also be emphasised that a potential as simple as the ABOP can never accurately describe all phases and properties of a material. Less important structures and properties must generally be sacrificed in favour of properties that are decisive for the phenomena and systems that the potential will be used to study. The accuracy of the potential can be assessed by calculating properties not included in the fitting, such as the melting temperature of the ground structure, surface energies, and formation energies of different defects, from a simple vacancy to various interstitial configurations.

In the following section, we will summarise three selected previous parametrisations in the ABOP form, to illustrate the above-explained fitting methodology and review the general accuracy of successful potentials. First, we look at the Pt-Pt potential by Albe et al., referenced above [3], and then the Fe-Fe and O-O potentials by Müller et al. [38], and Erhart et al. [20] used in the development of the Fe-O potential in this work.
3.2 Examples

3.2.1 Pt

The Pt-Pt ABOP \cite{Albe2004} was fitted to properties of different structures over a wide range of coordination numbers. Pt crystallises into the face centred cubic structure with the coordination number 12, for which experimental data is readily available. Lower coordinated structures (diamond, simple cubic, body centred cubic) were studied with DFT simulations, to get reference data for the bonding nature of differently coordinated atoms in solid Pt. The parameters $D_0$, $r_0$, $\beta$, and $S$ where chosen according to the dimer properties and the Pauling relation as described in the previous section. $D_0$, $r_0$, and $\beta$ were allowed to vary within the limits of experimental values from the literature, and $S$ was adjusted to satisfy the Pauling relation as well as possible for all reference structures. The remaining parameters in the bond order function were numerically fitted to describe the elastic properties well. The melting point was found to be strongly dependent on the cutoff range, so the cutoff parameters $R$ and $D$ were adjusted to reproduce an accurate melting temperature.

The full parameter set is given in Table \ref{tab:pt parameters}. A selected list of properties from the original publication obtained by the ABOP, compared to DFT and experimental results, is given in Table \ref{tab:pt properties}. The ABOP shows an excellent agreement with theoretical and experimental results, on par or better than other published Pt potentials (see the publication for a comparison \cite{Albe2004}).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_0$ (eV)</td>
<td>3.683</td>
</tr>
<tr>
<td>$r_0$ (Å)</td>
<td>2.384</td>
</tr>
<tr>
<td>$\beta$ (Å$^{-1}$)</td>
<td>1.64249</td>
</tr>
<tr>
<td>$S$</td>
<td>2.24297</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>8.542 × 10$^{-4}$</td>
</tr>
<tr>
<td>$c$</td>
<td>34.00</td>
</tr>
<tr>
<td>$d$</td>
<td>1.1</td>
</tr>
<tr>
<td>$h$</td>
<td>1.0</td>
</tr>
<tr>
<td>$2\mu$ (Å$^{-1}$)</td>
<td>2.67</td>
</tr>
<tr>
<td>$R$ (Å)</td>
<td>3.1</td>
</tr>
<tr>
<td>$D$ (Å)</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Table 3.1: The parameters for the Pt ABOP by Albe et al. \cite{Albe2004}.

26
<table>
<thead>
<tr>
<th></th>
<th>Theory (DFT)(^a)</th>
<th>Experiment(^a)</th>
<th>ABOP</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pt-Pt dimer</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(r_0) (Å)</td>
<td>2.40, 2.39</td>
<td>2.34</td>
<td>2.384</td>
</tr>
<tr>
<td>(E_{\text{coh}}) (eV)</td>
<td>-1.65, -1.97</td>
<td>-1.57, -1.855</td>
<td>-1.8415</td>
</tr>
<tr>
<td>(\omega_0) (cm(^{-1}))</td>
<td>218, 234</td>
<td>218, 259</td>
<td>236</td>
</tr>
<tr>
<td><strong>Diamond</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a) (Å)</td>
<td>5.807, 5.821</td>
<td>5.811</td>
<td></td>
</tr>
<tr>
<td>(V) (Å(^3))</td>
<td>24.48, 24.65</td>
<td>24.51</td>
<td></td>
</tr>
<tr>
<td>(E_{\text{coh}}) (eV)</td>
<td>-4.703, -4.587</td>
<td>-4.662</td>
<td></td>
</tr>
<tr>
<td>(B) (GPa)</td>
<td>123, 117</td>
<td>115.3</td>
<td></td>
</tr>
<tr>
<td>(B')</td>
<td>5.31, 5.57</td>
<td>5.15</td>
<td></td>
</tr>
<tr>
<td><strong>Simple cubic</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a) (Å)</td>
<td>2.652, 2.642</td>
<td>2.621</td>
<td></td>
</tr>
<tr>
<td>(V) (Å(^3))</td>
<td>18.66, 18.44</td>
<td>17.99</td>
<td></td>
</tr>
<tr>
<td>(E_{\text{coh}}) (eV)</td>
<td>-5.296, -5.277</td>
<td>-5.276</td>
<td></td>
</tr>
<tr>
<td>(B) (GPa)</td>
<td>182, 183</td>
<td>177.6</td>
<td></td>
</tr>
<tr>
<td>(B')</td>
<td>5.32, 5.53</td>
<td>5.39</td>
<td></td>
</tr>
<tr>
<td><strong>Body centred cubic</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a) (Å)</td>
<td>3.192, 3.166</td>
<td>3.094</td>
<td></td>
</tr>
<tr>
<td>(V) (Å(^3))</td>
<td>16.25, 15.86</td>
<td>14.81</td>
<td></td>
</tr>
<tr>
<td>(E_{\text{coh}}) (eV)</td>
<td>-5.641, -5.691</td>
<td>-5.276</td>
<td></td>
</tr>
<tr>
<td>(B) (GPa)</td>
<td>240, 246</td>
<td>245.5</td>
<td></td>
</tr>
<tr>
<td>(B')</td>
<td>5.25, 5.66</td>
<td>5.51</td>
<td></td>
</tr>
<tr>
<td><strong>Face centred cubic</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a) (Å)</td>
<td>3.992, 3.965</td>
<td>3.917</td>
<td>3.917</td>
</tr>
<tr>
<td>(V) (Å(^3))</td>
<td>15.91, 15.58</td>
<td>15.02</td>
<td>15.02</td>
</tr>
<tr>
<td>(E_{\text{coh}}) (eV)</td>
<td>-5.77, -5.77</td>
<td>-5.77</td>
<td>-5.77</td>
</tr>
<tr>
<td>(B) (GPa)</td>
<td>260, 265</td>
<td>288.4</td>
<td>282.6</td>
</tr>
<tr>
<td>(B')</td>
<td>5.4, 5.9</td>
<td>5.64</td>
<td></td>
</tr>
<tr>
<td>(c_{11}) (GPa)</td>
<td>358</td>
<td>351.5</td>
<td></td>
</tr>
<tr>
<td>(c_{12}) (GPa)</td>
<td>253</td>
<td>248.1</td>
<td></td>
</tr>
<tr>
<td>(c_{44}) (GPa)</td>
<td>77.4</td>
<td>89.5</td>
<td></td>
</tr>
<tr>
<td>(T_{\text{melt}}) (K)</td>
<td>2045</td>
<td>2100±20</td>
<td></td>
</tr>
<tr>
<td>(E_{\text{vac}}) (eV)</td>
<td>1.35</td>
<td>1.21</td>
<td></td>
</tr>
<tr>
<td>(E_{\text{cut}}) (eV)</td>
<td>3.5</td>
<td>5.34</td>
<td></td>
</tr>
<tr>
<td>(\gamma_{(100)}) (eV/Å(^2))</td>
<td>0.114</td>
<td>0.123</td>
<td></td>
</tr>
<tr>
<td>(\gamma_{(111)}) (eV/Å(^2))</td>
<td>0.092</td>
<td>0.091</td>
<td></td>
</tr>
<tr>
<td>(\gamma_{(110)}) (eV/Å(^2))</td>
<td>0.243</td>
<td>0.119</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)For references, see the original publication [3].

Table 3.2: Properties of Pt predicted by the ABOP and compared with theoretical and experimental studies. The listed properties are the equilibrium bond length \(r_0\), cohesive energy per atom \(E_{\text{coh}}\), vibration frequency \(\omega_0\), lattice constant \(a\), bulk modulus \(B\), and pressure derivative of the bulk modulus \(B'\). Additionally, for the fcc phase the elastic constants \(c_{ij}\), melting temperature \(T_{\text{melt}}\), formation \((E^f)\) and surface energies (\(\gamma\)) for different configurations are given.
3.2.2 Fe

The Fe-Fe ABOP by Müller et al. \[38\] was fitted using the same methodology as for the Pt potential. Experimental and theoretical properties for reference structures with coordination numbers from two (dimer) to twelve (close-packed structures) were used to guide the fitting parameters. Several EAM-like iron potentials had previously been published. The motivation behind developing another potential in the ABOP formalism is to, unlike previous potentials, correctly describe the phase transitions taking place at high temperatures in iron, while still maintaining a good description of the bulk, surface, and defect properties. The ground state of iron, bcc \(\alpha\)-iron transforms into the fcc phase (\(\gamma\)-iron) at 1184 K, and back to bcc (\(\delta\)-iron) at 1665 K, before melting. The driving force behind the phase transitions is the contributions of ferromagnetic energy to the total energy. At high temperatures, the impact of the degrees of freedom of the magnetic spins become strong enough to favour the fcc phase over the bcc phase. Since the classical interatomic potentials neglect electrons, reproducing these phase transitions presents a challenge. The goal was to mimic the contributions of the spin system purely by adjusting the lattice energy differences appropriately, and then monitoring the Gibbs free energy difference between the phases at the desired temperatures.

The parameter set obtained from the fitting is given in Table 3.3. Due to the small difference between the first and second nearest neighbour in bcc iron, the cutoff range was chosen to also include the second nearest neighbours. The parameter \(h\), determining the minimum of the angular function, was chosen to favour the bcc phase while keeping a good description of the elastic constants. The dimer properties had to be sacrificed in favour of more accurate surface energies, and the parameters \(D_0\) and \(r_0\) therefore deviate slightly from experimental results.

Table 3.4 shows selected properties of the reference structures, predicted by the ABOP and compared with theoretical and experimental results, taken from the original publication \[38\]. The overall agreement is good. Along with the previously mentioned \(\alpha\)-\(\gamma\)-\(\delta\) phase transitions, the Bain path is also well described by the ABOP. The Bain path in iron is the transformation path from bcc to fcc along a \(\langle 100\rangle\) direction as a result of elongation. The energy barrier for the Bain path transition is much closer to the reference value than previously published iron potentials (see the publication for a thorough comparison of properties between other potentials). A shortcoming of the potential, in addition to the dimer properties, is a very low linear expansion coefficient for bcc iron, which was accepted in favour of a good description
of the phase transitions. The surface energies are also consistently lower than the reference values, but still on par with other potentials. Formation energies for the vacancy and various interstitial configurations were also calculated and are in decent agreement with experimental and theoretical results.

### 3.2.3 O

The oxygen ABOP by Erhart et al. [20] was fitted to experimental data of the dimer and ozone molecules, as well as DFT results of different crystal structures over a wide coordination range (diamond to fcc). The dimer properties were used to fix the $D_0$, $r_0$, and the $\beta$ parameters according to the Pauling relation. The Pauling plot is showed in Figure 3.1. The $h$ parameter, specifying the preferred optimal angle between neighbouring atoms, was chosen according to the bond angle of the ozone molecule. The remaining parameters were numerically fitted to reproduce the reference data as well as possible. Two different values for the cutoff range were given, as seen in Table 3.5. The lower value, 2.1 Å, provides a good description of the ozone molecule, but overestimates the energies of the higher coordinated structures. Conversely, the alternative cutoff (2.6 Å) provides a better description of the higher coordinated structures at the expense of the ozone molecule. A comparison between the reference values and the values predicted by the ABOP is given in Table 3.6.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_0$ (eV)</td>
<td>1.5</td>
</tr>
<tr>
<td>$r_0$ (Å)</td>
<td>2.29</td>
</tr>
<tr>
<td>$\beta$ (Å$^{-1}$)</td>
<td>1.4</td>
</tr>
<tr>
<td>$S$</td>
<td>2.0693109</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>0.0115751</td>
</tr>
<tr>
<td>$c$</td>
<td>1.2898716</td>
</tr>
<tr>
<td>$d$</td>
<td>0.3413219</td>
</tr>
<tr>
<td>$h$</td>
<td>-0.26</td>
</tr>
<tr>
<td>$2\mu$ (Å$^{-1}$)</td>
<td>0.0</td>
</tr>
<tr>
<td>$R$ (Å)</td>
<td>3.15</td>
</tr>
<tr>
<td>$D$ (Å)</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Table 3.3: The parameters for the Fe ABOP by Müller et al. [38].
<table>
<thead>
<tr>
<th></th>
<th>Theory (DFT)</th>
<th>Experiment</th>
<th>ABOP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-Fe dimer</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( r_0 ) (Å)</td>
<td>2.01</td>
<td>2.02</td>
<td>2.29</td>
</tr>
<tr>
<td>( E_{\text{coh}} ) (eV)</td>
<td>-1.65</td>
<td>-1.04, -1.14</td>
<td>-1.50</td>
</tr>
<tr>
<td>( \omega_0 ) (cm(^{-1}))</td>
<td>397</td>
<td>299</td>
<td>239</td>
</tr>
<tr>
<td>Diamond</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( a ) (Å)</td>
<td>4.856</td>
<td>5.557</td>
<td></td>
</tr>
<tr>
<td>( \Delta E ) (eV)</td>
<td>1.17</td>
<td>2.13</td>
<td></td>
</tr>
<tr>
<td>Simple cubic</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( a ) (Å)</td>
<td>2.367</td>
<td>2.417</td>
<td></td>
</tr>
<tr>
<td>( \Delta E ) (eV)</td>
<td>0.75</td>
<td>1.15</td>
<td></td>
</tr>
<tr>
<td>Body centred cubic</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( a ) (Å)</td>
<td>2.832</td>
<td>2.860</td>
<td>2.860</td>
</tr>
<tr>
<td>( E_{\text{coh}} ) (eV)</td>
<td>-4.28</td>
<td>-4.28</td>
<td>-4.280</td>
</tr>
<tr>
<td>( B ) (GPa)</td>
<td>189</td>
<td>169</td>
<td>169</td>
</tr>
<tr>
<td>( B' )</td>
<td>5.1</td>
<td></td>
<td>4.6</td>
</tr>
<tr>
<td>( c_{11} ) (GPa)</td>
<td>277</td>
<td>226</td>
<td>225</td>
</tr>
<tr>
<td>( c_{12} ) (GPa)</td>
<td>147</td>
<td>140</td>
<td>142</td>
</tr>
<tr>
<td>( c_{44} ) (GPa)</td>
<td>96</td>
<td>116</td>
<td>126</td>
</tr>
<tr>
<td>( T_{\text{melt}} ) (K)</td>
<td>1811</td>
<td>2270±20</td>
<td></td>
</tr>
<tr>
<td>( E^*_{\text{f}} ) (eV)</td>
<td></td>
<td>1.59-1.89</td>
<td>1.56</td>
</tr>
<tr>
<td>( E^*_{\text{m}} ) (eV)</td>
<td></td>
<td>0.55</td>
<td>0.57</td>
</tr>
<tr>
<td>( \gamma_{(100)} ) (meV/Å(^2))</td>
<td>143</td>
<td>150</td>
<td>104</td>
</tr>
<tr>
<td>( \gamma_{(110)} ) (meV/Å(^2))</td>
<td>142</td>
<td>150</td>
<td>85</td>
</tr>
<tr>
<td>( \gamma_{(111)} ) (meV/Å(^2))</td>
<td>157</td>
<td>150</td>
<td>115</td>
</tr>
<tr>
<td>Face centred cubic</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( a ) (Å)</td>
<td>3.482</td>
<td>3.562</td>
<td>3.611</td>
</tr>
<tr>
<td>( \Delta E ) (eV)</td>
<td>0.11, 0.06</td>
<td>0.030</td>
<td></td>
</tr>
<tr>
<td>( B ) (GPa)</td>
<td>199</td>
<td>133</td>
<td>164</td>
</tr>
<tr>
<td>( B' )</td>
<td>5.5</td>
<td></td>
<td>4.6</td>
</tr>
<tr>
<td>( c_{11} ) (GPa)</td>
<td>309</td>
<td>154</td>
<td>204</td>
</tr>
<tr>
<td>( c_{12} ) (GPa)</td>
<td>152</td>
<td>122</td>
<td>144</td>
</tr>
<tr>
<td>( c_{44} ) (GPa)</td>
<td>201</td>
<td>77</td>
<td>101</td>
</tr>
<tr>
<td>Hexagonal close packed</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( a ) (Å)</td>
<td>2.459</td>
<td>2.555</td>
<td></td>
</tr>
<tr>
<td>( c/a )</td>
<td>1.58</td>
<td>1.63</td>
<td></td>
</tr>
<tr>
<td>( \Delta E ) (eV)</td>
<td>0.06</td>
<td>0.027</td>
<td></td>
</tr>
</tbody>
</table>

\( ^{a} \)For references, see the original publication [38].

Table 3.4: Properties of Fe predicted by the ABOP and compared with theoretical and experimental studies. The listed properties are the equilibrium bond length \( r_0 \), cohesive energy per atom \( E_{\text{coh}} \), energy difference from the ground state (bcc) \( \Delta E \), vibration frequency \( \omega_0 \), lattice constant \( a \), bulk modulus \( B \), pressure derivative of the bulk modulus \( B' \), and elastic constants \( c_{ij} \). Additionally, for the bcc phase, the melting temperature \( T_{\text{melt}} \), vacancy formation and migration energies (\( E^*_{\text{f}}, E^*_{\text{m}} \)), and surface energies \( \gamma \) are given.
Figure 3.1: The semi-logarithmic Pauling plot, relating the bond energy to the bond length, for oxygen \[20\].

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_0$ (eV)</td>
<td>5.166</td>
</tr>
<tr>
<td>$r_0$ (Å)</td>
<td>1.2075</td>
</tr>
<tr>
<td>$\beta$ (Å$^{-1}$)</td>
<td>2.3090</td>
</tr>
<tr>
<td>$S$</td>
<td>1.3864</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>0.82595</td>
</tr>
<tr>
<td>$c$</td>
<td>0.035608</td>
</tr>
<tr>
<td>$d$</td>
<td>0.046496</td>
</tr>
<tr>
<td>$h$</td>
<td>0.45056</td>
</tr>
<tr>
<td>$2\mu$ (Å$^{-1}$)</td>
<td>0.0</td>
</tr>
<tr>
<td>$R$ (Å)</td>
<td>2.10 or 2.60</td>
</tr>
<tr>
<td>$D$ (Å)</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Table 3.5: The parameters for the oxygen ABOP by Erhart et al. \[20\].
<table>
<thead>
<tr>
<th></th>
<th>Theory (DFT)(^a)</th>
<th>Experiment(^a)</th>
<th>ABOP</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>O-O dimer</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(r_0) (Å)</td>
<td>1.21</td>
<td>1.21</td>
<td>1.21</td>
</tr>
<tr>
<td>(E_{\text{coh}}) (eV)</td>
<td>-2.85</td>
<td>-2.58</td>
<td>-2.58</td>
</tr>
<tr>
<td><strong>Ozone, ground state</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(r_b) (Å)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\theta) (deg)</td>
<td>116.0</td>
<td>116.8</td>
<td>116.8(178.7)</td>
</tr>
<tr>
<td>(\Delta E) (eV)</td>
<td>0.47</td>
<td>0.49</td>
<td>0.50 (0.83)</td>
</tr>
<tr>
<td><strong>Ozone, equilateral triangle (ring)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(r_b) (Å)</td>
<td>1.28</td>
<td>1.28</td>
<td>1.40</td>
</tr>
<tr>
<td>(\Delta E) (eV)</td>
<td>0.47</td>
<td>0.49</td>
<td>0.50 (0.83)</td>
</tr>
<tr>
<td><strong>O(_4) molecule</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(r_b) (Å)</td>
<td>1.80</td>
<td>1.81</td>
<td></td>
</tr>
<tr>
<td>(\Delta E) (eV)</td>
<td>2.26</td>
<td>1.81</td>
<td></td>
</tr>
<tr>
<td><strong>Graphene sheet</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(r_b) (Å)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\Delta E) (eV)</td>
<td>1.60</td>
<td>1.60</td>
<td></td>
</tr>
<tr>
<td><strong>Diamond</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a) (Å)</td>
<td>2.50</td>
<td>2.07 (2.15)</td>
<td></td>
</tr>
<tr>
<td>(\Delta E) (eV)</td>
<td>2.49</td>
<td>2.08 (2.17)</td>
<td></td>
</tr>
<tr>
<td><strong>Simple cubic</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a) (Å)</td>
<td>2.91</td>
<td>2.43 (2.76)</td>
<td></td>
</tr>
<tr>
<td>(\Delta E) (eV)</td>
<td>2.32</td>
<td>2.12 (2.27)</td>
<td></td>
</tr>
<tr>
<td><strong>Body centred cubic</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a) (Å)</td>
<td>3.65</td>
<td>3.03 (3.54)</td>
<td></td>
</tr>
<tr>
<td>(\Delta E) (eV)</td>
<td>2.29</td>
<td>2.14 (2.31)</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)For references, see the original publication [20].

Table 3.6: Properties of O predicted by the ABOP and compared with theoretical and experimental studies. The listed properties are the equilibrium bond length \(r_0\) (or \(r_b\)), cohesive energy per atom \(E_{\text{coh}}\), energy difference from the dimer \(\Delta E\), lattice constant \(a\). Values given in parentheses are calculated using the extended cutoff 2.6 Å.
4 Fitting of the Fe-O potential

4.1 Data used in the fitting

Iron oxides occur widely in nature, from minerals in the Earth’s mantle to being a main ingredient of rust, and are broadly used in industrial and medical applications [17]. Experimental and theoretical studies on different properties of the iron oxides are therefore continuously being carried out in material physics research. The mobility of oxygen impurities in pure solid iron has also recently been increasingly studied. Impurities, such as oxygen, are always present in iron-based materials, either for alloying purposes or as natural impurities. For instance, oxide-dispersion strengthened (ODS) steels are being studied as possible candidates for materials in new generations of fusion and fission reactors, due to their high temperature tolerance and increased irradiation resistance. In ODS steels, small nano-sized Y-O(-Ti) particles are allowed to precipitate within the steel structure. The mobility of oxygen in the iron/steel crystal is essential for understanding the precipitation and growth of the nanoparticles. It is therefore of interest to develop an interatomic potential for the Fe-O system that could describe the most common iron oxides, as well as allow for large-scale simulations of the behaviour of oxygen solutes in iron and iron-based materials. The existing reactive force field for Fe-O is capable of predicting the thermodynamics of the common iron oxides [4], but performs poorly for oxygen defects and cannot be used for studying single oxygen impurities in iron [13]. A complete Fe-O potential requires parametrisations for the interactions Fe-O, Fe-Fe, and O-O. The existing ABOPs for pure iron and oxygen presented in the previous section can be used to describe the Fe-Fe and O-O interactions, and only an ABOP parametrisation for the Fe-O interactions is missing.

The phase diagram of the iron oxygen system is shown in Figure 4.1 [44]. Iron oxides exist in nature in mainly three different mineral forms; magnetite, wüstite, and hematite. At low temperatures and oxygen concentrations, the oxygen crystallises into magnetite (Fe$_3$O$_4$) mixed together with pure α-Fe. Wüstite (Fe$_{1-x}$O) is stable at temperatures above around 850 K and oxygen concentrations slightly above 50 at.%. Hematite (Fe$_2$O$_3$) is stable at the corresponding oxygen concentration.

Wüstite (Fe$_{1-x}$O) crystallises into an iron deficient simple cubic (NaCl) structure. Equivalently, it can be seen as two interpenetrating face centred cubic structures of Fe$^{2+}$ and O$^{2+}$ ions, with a number of vacant iron sites. For charge neutrality, some iron cations oxidise to Fe$^{3+}$ cations, which have been shown to occupy the normally
Figure 4.1: The phase diagram of Fe-O. On the left is the full phase diagram, and on the right a closer image of the different iron oxide phases [44].

vacant tetrahedral sites. The value of $1 - x$ in Fe$_{1-x}$O ranges from 0.83 to 0.95 [17]. Stoichiometric FeO is not stable at low pressures. The lattice parameter is between 4.28-4.33 Å, depending on the vacancy content. When cooled slowly below 853 K, the structure dissolves into pure Fe and Fe$_3$O$_4$. Rapid quenching can, however, result in a metastable Fe$_{1-x}$O phase [17]. The effect of non-stoichiometry, i.e. the value of $x$, has been shown to strongly affect the elastic properties. The bulk modulus of wüstite has been extensively studied experimentally and is fairly insensitive to the non-stoichiometry in the range $0.90 < 1 - x < 0.98$, which represent typical experimental samples. In that range, the reported values for the bulk modulus are around 144–152 GPa. However, motivated by a much higher theoretically predicted value for ideal stoichiometric FeO, Zhang prepared samples with $1 - x \approx 0.99$ and found that the bulk modulus for near-stoichiometric wüstite is indeed significantly higher (175 GPa) than for typical defect concentrations [58]. The effects of non-stoichiometry on elasticity is important to keep in mind when gathering reference data for the potential fitting database, as we only consider ideal FeO in the numerical fitting. As a reference value for the bulk modulus of ideal FeO, we use the value reported by Zhang for Fe$_{0.99}$O. The wide array of experimentally determined elastic constants available for wüstite must also either be scaled towards the stoichiometric
bulk modulus, or not included in the fitting database at all, since the experimental samples typically consist of Fe_{0.94−0.95}O.

Magnetite (Fe_3O_4) crystallises into an inverse spinel structure. Oxygen ions are ordered in a face centred cubic structure, with the octahedral and tetrahedral sites partly filled with Fe cations. The cation ratio Fe^{2+}/Fe^{3+} is 1/2. Reliable experimental results for the elastic properties are available from single crystal Fe_3O_4 studies.

Hematite (α-Fe_2O_3) has the same crystal structure as Corundum (Al_2O_3). The oxygen ions are ordered in a hexagonal close packed cell, with 2/3 of the octahedral sites filled with Fe^{3+} ions. The Fe^{3+} arrangement produces pairs of distorted Fe(O)_6 octahedra, with half of the Fe-O bonds in the octahedron slightly longer than the other. Hematite has been extensively studied experimentally and reference values for the elasticity and compressibility are readily available, although the value of i.e. the bulk modulus vary strongly from study to study (170−230 GPa).

Reference values for the cohesive or formation energies can be obtained from the experimental enthalpies of formation (measured at room temperatures). At normal pressures, the enthalpy is approximately the same as the internal potential energy, \( H = U + PV \approx U \). In the formation of a compound A_mB_n, the relation between the cohesive energies (per atom) is

\[
E_f = E_p(A_mB_n) - mE_{coh}(A) - nE_{coh}(B)
\]  \hspace{1cm} (4.1)

where \( E_p(A_mB_n) \) is the potential energy of \( A_mB_n \), and \( E_{coh} \) the cohesive energies of the ground states of A and B. The formation energies for the different iron oxides together with the other structural and mechanical properties are listed in Table 4.2.

As the mobility and energetics of oxygen solutes are of interest, defect and migration properties of oxygen in α-Fe must be either included in the reference database of the fitting process, or compared to when testing the potential. First principles calculations on oxygen atoms in iron have been carried out in a number of studies \([5,6,16,24,29,49]\). Oxygen has a very low solubility in defect-free iron. The octahedral interstitial site in bcc iron is preferred over the tetrahedral site, with both being heavily favoured over substitutional oxygen atoms. The formation energies for the different oxygen point defects are listed in Table 4.2. It has been shown that the presence of vacancies in the iron lattice has a strong effect on the solubility and mobility of oxygen \([24]\). Compared to other solutes, oxygen atoms form strong bonds with nearby vacancies in iron. The vacancy concentration therefore essentially controls the solubility of oxygen, allowing the oxygen concentration to reach that of the vacancies
by forming oxygen-vacancy (O-V) bonds. The strong O-V bonds also reduce the mobility of the interstitial oxygen solutes. Octahedral oxygen atoms in a vacancy-free iron lattice migrate to another octahedral site, passing through the tetrahedral site with a migration barrier of 0.48—0.60 eV \[16,24,49\]. If, however, the oxygen atom has a nearest-neighbour vacancy, the O-V pair has been shown to migrate together as a pair in a two-step process \[24\]. The vacancy then first moves to a nearby lattice site (or, a nearby Fe atom jumps to the vacant site), and the oxygen atom then quickly reconnects with the vacancy at its nearest-neighbour octahedral site. The energy barrier for this two-step O-V migration is significantly higher (1.55 eV \[24\]) than for single oxygen migration in a perfect iron lattice. The binding energy of the O-V pair has been calculated for bond lengths longer than the first nearest-neighbour distance, and was found to be significantly strong also for second nearest-neighbour distances \[16,49\]. The binding energies and diffusion mechanisms for clusters with multiple vacancies or oxygen atoms (\(V_nO_m\)) in iron have also been studied recently in first principles calculations \[5,6\].
4.2 Fitting approach

The fitting of the Fe-O ABOP was carried out with the code TULIP [25]. Figure 4.2 shows an overview of the steps involved in the fitting of the potential parameters. The physical properties of the different structures are given as target values. The values for all included properties are then calculated using the parameter values set as the initial guess. The structural properties, i.e. the cohesive or formation energy, lattice constants, and optionally, bond angles and bond lengths are determined by a Molecular Dynamics (MD) relaxation simulation. A simplified illustration of the MD algorithm is shown in Figure 4.3. The coordinates of all individual atoms are given for all structures included in the fitting process. In MD, the forces acting on each atom are calculated using the potential energy function, which allows the movement of the atoms in a small time step to be calculated according to classical equations of motion. Repeatedly solving the equations of motion allows one to simulate the evolution of the system over a given period of time. When calculating the structural properties, the structures are allowed to relax over a sufficiently long time, i.e. the atoms are allowed to find their equilibrium positions. The equilibrium lattice constant(s) and cohesive energy of the atoms in the structure can then be directly extracted along with the thermodynamic properties of the system (temperature, pressure, volume). In the calculation of the formation energy in the fitting code, the cohesive energies of the given ground state structures of the present elements are first obtained by separate initial MD relaxations. The formation energy of the structural compound can then be calculated according to Equation 4.1.

The bulk modulus is calculated by straining the equilibrium structure in all directions. The bulk modulus can then be determined by fitting the obtained volume-energy data to the Birch-Murnaghan equation of state [7,37]. Similarly, the different elastic constants are calculated by applying the corresponding strain matrix to the structure, and using the obtained strain-energy data in a fit to a polynomial from which the elastic constant can be extracted. When the needed properties are obtained, the parameters are updated in a minimisation step. The fitting code attempts to minimise the merit/cost function, i.e. the function measuring the agreement between the calculated properties and the reference target values. The merit/cost function contains a term with the difference between predicted and target properties, and a term with the fitting parameters. The calculation of properties followed by a minimisation step is iterated until the given convergence criteria are met. Weights can be put on the more important properties to guide the fit. In TULIP, the minimisation can be...
carried out with a number of different optimisation algorithms. The implemented algorithms are listed in Table 4.1. The fitting of the Fe-O potential was mostly done with the Levenberg-Marquardt method, Powell’s dog-leg method, and the Simplex method.
Set initial atom coordinates and velocities $r_i(t = 0), v_i(t = 0)$

Get forces, $F_i = -\nabla U(r_i)$

Move atoms according to equations of motion, $r_i(t) \rightarrow r_i(t + \Delta t)$, $v_i(t) \rightarrow v_i(t + \Delta t)$

Calculate physical quantities

Move time forward, $t = t + \Delta t$

$t > t_{max}$?

Yes: Finish, output final results

No: $t > t_{max}$?

Figure 4.3: A simplified flowchart of the algorithm in Molecular Dynamics simulations.

---

Conjugate gradient method
Powell’s method
Gauss-Newton method
Levenberg-Marquardt method
Powell’s dog-leg method
Simulated annealing
Simplex method
Differential evolution
Particle swarm method
Bee colony method
Gravitational search

Table 4.1: Implemented optimisation algorithms in the fitting code TULIP [25].
4.3 Results and discussion

Table 4.2 shows the properties of the different iron oxide structures used in the fitting and discussed in section 4.1, as well as the values predicted by different ABOP parametrisations. In ABOP 1, all parameters were fitted simultaneously, including the specific three-body $\alpha$ and $\omega$ parameters (see Equation 2.65). The result is a parametrisation that agrees well with the highest prioritised reference target values (formations energies, lattice constants), but which severely overestimates the dimer bond energy. The point defect energies of oxygen atoms in iron are also in excellent agreement with the target values. The bulk moduli for magnetite and hematite deviate significantly from the experimental values, but agree well for wüstite. However, further testing revealed a number of critical flaws. First of all, the predicted ground state of FeO is not the NaCl-structured wüstite ($Z = 6$), but instead the lower coordinated ($Z = 4$) ZnS and wurtzite phases (by about 0.4 eV in cohesive energy). The favouring of lower coordinated structures can be understood by the gross overestimation of the dimer bond energy, leading to higher energies per bond for low coordinations. Relaxing the wüstite structure with ABOP 1 in an MD simulation eventually results in a collapse to the ZnS structure. Secondly, heating of the magnetite structure leads to the Fe atoms starting to move towards positions of lower energy, and after complete melting and subsequent quenching, the frozen amorphous structure is lower in energy than crystalline magnetite. The drawbacks of ABOP 1 illustrate the importance of testing the potential after a seemingly promising parametrisation from the fitting routine. ABOP 1 should not be used in any simulations and is here only shown as an example highlighting the challenges needed to overcome in order to get a good Fe-O potential.

ABOP 2 is a result of fitting the Fe-O interaction only, setting all Fe-Fe interactions to zero. With no Fe-Fe bonds affecting the potential energy, the Pauling relation can be used for the individual Fe-O bonds in the different structures to fix the Morse parameters $D_0$, $r_0$, $\beta$, and $S$. In hematite and magnetite, the second nearest Fe-O distance is also within the cutoff radius, making the Pauling study slightly less straightforward than in the case of a nearest-neighbour model, as described in section 3.1, where the bond energies are directly obtained from the cohesive energies. With second nearest neighbour bonds, the individual bond energies are not known based on the experimental cohesive energies. Determining the Morse parameters can then be achieved by looking at parameter values for which the criterion $N_1E_b(r_1) + N_2E_b(r_2) = E_{coh}$ is fulfilled (where $E_b(r) = D_0e^{-\beta S\sqrt{2S}}$), i.e. parameter values where the sum of the individual bond energies adds up to the known cohesive energies.
### Table 4.2: Experimental and DFT literature values for properties of different iron oxides and oxygen defects, compared with values predicted by the ABOP parametrisations.

<table>
<thead>
<tr>
<th>Property</th>
<th>Theory (DFT)</th>
<th>Experiment</th>
<th>ABOP 1</th>
<th>ABOP 2</th>
<th>ABOP 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-O dimer</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( r_0 ) (Å)</td>
<td>1.614(^a)</td>
<td>1.619(^b)</td>
<td>1.553</td>
<td>1.62</td>
<td>1.58</td>
</tr>
<tr>
<td>( E_b ) (eV)</td>
<td>5.47(^a)</td>
<td>4.13–4.21(^b)</td>
<td>8.04</td>
<td>5.04</td>
<td>7.93</td>
</tr>
<tr>
<td>FeO wüstite (( Fm\overline{3}m ), no. 225)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( a ) (Å)</td>
<td>4.31(^a)</td>
<td>4.31(^c)</td>
<td>4.31</td>
<td>4.28</td>
<td>4.31</td>
</tr>
<tr>
<td>( E_f ) (eV/atom)</td>
<td>-1.40(^d)</td>
<td>-1.41(^d)</td>
<td>-1.40(^*)</td>
<td>-1.46</td>
<td></td>
</tr>
<tr>
<td>( E_{coh} ) (eV/atom)</td>
<td>-4.83</td>
<td>-4.84</td>
<td>-4.83(^*)</td>
<td>-4.86</td>
<td>-4.84</td>
</tr>
<tr>
<td>( B ) (GPa)</td>
<td>175(^c)</td>
<td>177</td>
<td>188</td>
<td>182</td>
<td></td>
</tr>
<tr>
<td>( c_{11} )</td>
<td>217–246(^e)</td>
<td>520</td>
<td>370</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( c_{12} )</td>
<td>121–149(^e)</td>
<td>23</td>
<td>52</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( c_{44} )</td>
<td>44–50(^f)</td>
<td>8</td>
<td>47</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe(_3)O(_4) magnetite (( Fd\overline{3}m ), no. 227)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( a )</td>
<td>8.39(^f)</td>
<td>8.44</td>
<td>8.38</td>
<td>8.58</td>
<td></td>
</tr>
<tr>
<td>( E_f )</td>
<td>-1.66(^d)</td>
<td>-1.67</td>
<td>-1.44</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( E_{coh} )</td>
<td>-4.96</td>
<td>-4.98</td>
<td>-4.98</td>
<td>-4.70</td>
<td></td>
</tr>
<tr>
<td>( B )</td>
<td>185.7(^g)</td>
<td>102</td>
<td>157</td>
<td>101</td>
<td></td>
</tr>
<tr>
<td>( c_{11} )</td>
<td>260.5(^h)</td>
<td>157</td>
<td>359</td>
<td>198</td>
<td></td>
</tr>
<tr>
<td>( c_{12} )</td>
<td>148.3(^g)</td>
<td>68</td>
<td>29</td>
<td>37</td>
<td></td>
</tr>
<tr>
<td>( c_{44} )</td>
<td>63.3(^g)</td>
<td>34</td>
<td>38</td>
<td>24</td>
<td></td>
</tr>
<tr>
<td>Fe(_2)O(_3) hematite (( R\overline{3}c ), no. 167)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( a )</td>
<td>5.035(^b)</td>
<td>5.09</td>
<td>5.05</td>
<td>5.21</td>
<td></td>
</tr>
<tr>
<td>( c )</td>
<td>13.747(^b)</td>
<td>13.40</td>
<td>13.91</td>
<td>12.98</td>
<td></td>
</tr>
<tr>
<td>( E_f )</td>
<td>-1.71(^d)</td>
<td>-1.74</td>
<td>-1.48</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( E_{coh} )</td>
<td>-4.97</td>
<td>-5.0</td>
<td>-4.91</td>
<td>-4.70</td>
<td></td>
</tr>
<tr>
<td>( B )</td>
<td>178(^i)</td>
<td>225(^i)</td>
<td>174</td>
<td>187</td>
<td></td>
</tr>
<tr>
<td>( c_{11} )</td>
<td>242(^j)</td>
<td>240</td>
<td>281</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( c_{12} )</td>
<td>55(^j)</td>
<td>71</td>
<td>122</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( c_{13} )</td>
<td>16(^j)</td>
<td>134</td>
<td>119</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( c_{33} )</td>
<td>228(^j)</td>
<td>221</td>
<td>231</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( c_{14} )</td>
<td>-13(^j)</td>
<td>-24</td>
<td>4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( c_{44} )</td>
<td>85(^j)</td>
<td>130</td>
<td>68</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( E_f ) (octahedral O in (\alpha)-Fe)</td>
<td>-0.38(^k)</td>
<td>-0.36</td>
<td>-</td>
<td>-0.38</td>
<td></td>
</tr>
<tr>
<td>( E_f ) (tetrahedral O in (\alpha)-Fe)</td>
<td>0.13(^k)</td>
<td>0.13</td>
<td>-</td>
<td>0.13</td>
<td></td>
</tr>
<tr>
<td>( E_f ) (substitutional O in (\alpha)-Fe)</td>
<td>1.06(^l)</td>
<td>1.28(^l)</td>
<td>1.27</td>
<td>1.22</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Ref. [39], \(^b\) Ref. [34], \(^c\) Ref. [58], \(^d\) Ref. [1], \(^e\) Ref. [28], \(^f\) Ref. [57], \(^g\) Ref. [17], \(^h\) Ref. [21], \(^i\) Ref. [48], \(^j\) Ref. [27], \(^k\) Ref. [16], \(^l\) Calculated using the difference between \( E_f^{\text{sub}} \) and \( E_f^{\text{octa}} \) from Ref. [6] and Ref. [36] compared with the \( E_f^{\text{octa}} \) from Ref. [16] used above.

Unstable, collapses into the ZnS structure.

---

\( r_0 \): dimer bond length, \( E_b \): dimer bond energy, \( a, c \): lattice constants, \( E_f \): formation energy, \( E_{coh} \): cohesive energy, \( B \): bulk modulus, and \( c_{ij} \): elastic constants.
<table>
<thead>
<tr>
<th></th>
<th>ABOP 1</th>
<th>ABOP 2</th>
<th>ABOP 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_0$</td>
<td>8.0792336359</td>
<td>5.0488363056</td>
<td>7.9851367774</td>
</tr>
<tr>
<td>$r_0$</td>
<td>1.5394516821</td>
<td>1.6184405579</td>
<td>1.5555688567</td>
</tr>
<tr>
<td>$\beta$</td>
<td>1.2487061420</td>
<td>1.5252155894</td>
<td>1.2135035992</td>
</tr>
<tr>
<td>$S$</td>
<td>2.6999064315</td>
<td>1.0233887244</td>
<td>2.8735224898</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>0.9871705059</td>
<td>0.0099834852</td>
<td>1.1742630926</td>
</tr>
<tr>
<td>$c$</td>
<td>19.9034513464</td>
<td>0.7141135805</td>
<td>19.8656293772</td>
</tr>
<tr>
<td>$d$</td>
<td>4.2366360696</td>
<td>1.2946420654</td>
<td>4.5750149838</td>
</tr>
<tr>
<td>$h$</td>
<td>0.5493064256</td>
<td>0.7995627757</td>
<td>0.0904310711</td>
</tr>
<tr>
<td>$R$</td>
<td>3.15</td>
<td>3.15</td>
<td>3.15</td>
</tr>
<tr>
<td>$D$</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
</tr>
<tr>
<td>$b_f$</td>
<td>10.0</td>
<td>10.0</td>
<td>10.0</td>
</tr>
<tr>
<td>$r_f$</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>$\alpha_{\text{Fe-Fe-O}}$</td>
<td>1.1284110670</td>
<td>0.0</td>
<td>1.0854004606</td>
</tr>
<tr>
<td>$\alpha_{\text{Fe-O-Fe}}$</td>
<td>0.3195721653</td>
<td>0.0</td>
<td>0.3316469057</td>
</tr>
<tr>
<td>$\alpha_{\text{Fe-O-O}}$</td>
<td>3.4956639678</td>
<td>0.0</td>
<td>3.4803491740</td>
</tr>
<tr>
<td>$\alpha_{\text{O-Fe-Fe}}$</td>
<td>1.0792155131</td>
<td>0.0</td>
<td>1.0361635661</td>
</tr>
<tr>
<td>$\alpha_{\text{O-Fe-O}}$</td>
<td>0.7546312148</td>
<td>0.0</td>
<td>0.7546312148</td>
</tr>
<tr>
<td>$\alpha_{\text{O-O-Fe}}$</td>
<td>-0.4471274847</td>
<td>0.0</td>
<td>0.001</td>
</tr>
<tr>
<td>$\omega_{\text{Fe-Fe-O}}$</td>
<td>0.8102961625</td>
<td>1.0</td>
<td>0.9201732967</td>
</tr>
<tr>
<td>$\omega_{\text{Fe-O-Fe}}$</td>
<td>0.6590800084</td>
<td>1.0</td>
<td>0.6842003046</td>
</tr>
<tr>
<td>$\omega_{\text{Fe-O-O}}$</td>
<td>1.0181922838</td>
<td>1.0</td>
<td>1.0988780255</td>
</tr>
<tr>
<td>$\omega_{\text{O-Fe-Fe}}$</td>
<td>0.9599638791</td>
<td>1.0</td>
<td>0.9823723952</td>
</tr>
<tr>
<td>$\omega_{\text{O-Fe-O}}$</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>$\omega_{\text{O-O-Fe}}$</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Table 4.3: ABOP parameters for the different Fe-O potentials. The Fe-Fe and O-O parameters by Müller et al. and Erhart et al., respectively, are given in in Table 3.3 and 3.5. Note that in ABOP 2, the Fe-Fe interactions are set to zero. In ABOP 3, the repulsive potential in Equations 2.67-2.68 was used for the Fe-Fe potential with $b_f = 2.9$, $r_f = 0.95$. 

42
energy.

Initially, the parameters $D_0$ and $r_0$ were set to the experimental dimer bond energy and bond distance, and $\beta$ and $S$ optimised to give bond energies corresponding to the known cohesive energies (calculated from the experimental formation energies). However, the obtained value of $\beta$, which has a direct effect on the predicted elastic properties, resulted in bulk moduli much lower than the reference values for all considered structures. On the other hand, fixing $\beta$ to a value corresponding to a more reasonable bulk moduli, forces $S$ to a value below 1.0 to satisfy the Pauling relation, which as evident in Equation 2.61 cannot be allowed. The dimer bond energy, $D_0$, was therefore increased to 5.0, allowing for better $\beta$ and $S$ values. However, increasing $D_0$ naturally also has an effect on the lower coordinated structures, leading to not only an overestimation of the dimer bond energy, but also the bond energies of the four-coordinated ZnS and Wurtzite structures. These structures are therefore (again) incorrectly the ground structures of FeO in the ABOP 2 parametrisation (about 0.3 eV lower in cohesive energy). The alternative would, as previously mentioned, have been to allow unphysically low bulk moduli due to a low value of $\beta$. Using the obtained Morse parameters as starting guesses, the remaining three-body parameters were fit using TULIP. The Morse parameters were also allowed to vary slightly around the values obtained from the Pauling study. The resulting best fit, shown as ABOP 2 in Table 4.2 predicts formation energies and lattice constants in good agreement with the reference values. The bulk moduli are also in reasonable agreement with the target values, as well as the elastic constants of hematite (except for $c_{13}$). The elastic constants for wüstite and magnetite are not well reproduced. With no Fe-Fe interactions along with the incorrect ground state of FeO, ABOP 2 is very limited in its usefulness. While simulations of e.g. oxygen impurities in iron, or coexisting iron and iron oxide phases cannot be performed using ABOP 2, it might in rare cases be applicable to studies of pure iron oxide structures.

The logical next step towards a full Fe-O potential, including Fe-Fe interactions, would be to subtract the total energy of the Fe-Fe interactions for all structures, and apply the Pauling bond analysis on the remaining Fe-O bond energies needed to reach the total cohesive energies of the structures. However, the contributions from the pure Fe potential are significantly different for the considered structures. Figure 4.4 shows the Pauling plot with Fe-Fe interactions ignored (ABOP 2) and with the Fe-Fe interactions subtracted. The Fe-Fe contribution to the total energy in wüstite is clearly higher than in hematite and magnetite, resulting in much steeper line when fitting the Pauling parameters. The dimer along with other lower coordinated
structures, such as wurtzite, were already overestimated in ABOP 1 and 2, and would now be severely overestimated with a fit to the bond energies of wüstite, hematite, and magnetite. Attempts were made to compensate for the effects of the Fe-Fe interactions by fitting all the three-body $\alpha$ and $\omega$ parameters, but without noteworthy results.

Given the challenges in achieving a good description of all the common iron oxide structures, ABOP 3 was fitted with the main focus on the oxygen point defects in iron, with only the wüstite structure along with the defect structures included in the fitting process. ABOP 3 was obtained by starting from the parameters of ABOP 1, and forcing the four-coordinated ZnS and wurtzite structures to be energetically more unstable than wüstite (which consequently also made hematite and magnetite more unstable), while fitting the defect formation energies and the properties of wüstite. As seen in Table 4.2, the agreement with the reference data is good apart from the elastic constants $c_{11}$ and $c_{12}$. Attempts to get a better agreement for $c_{11}$ and $c_{12}$ resulted in the ZnS and wurtzite structures again becoming the ground structure of FeO. Note that while the energies for magnetite and hematite are not drastically overestimated, neither structure can reliably be simulated with ABOP 3. Both magnetite and hematite are stable at zero temperature, but melt already in room temperature.
simulations.

To test ABOP 3, various other defect configurations in bcc iron, beyond the single oxygen defects, were calculated and compared with published DFT results. As discussed in Section 4.1, the presence of vacancies has a strong effect on the diffusion of oxygen in iron due to the relatively strong O-V bonds. Apart from the binding energies between oxygen and vacancies, Barouh et al. have also calculated binding energies for clusters with multiple vacancies and/or oxygen interstitials in iron [5,6]. They showed that also the binding energies for O\textsubscript{V}\textsubscript{2}, and particularly O\textsubscript{2}V defects are significant. The most stable O\textsubscript{2}V configuration in iron has a binding energy similar to that of the O-V bond. The binding energy between two defect clusters \(X_nY_m\) and \(X'_nY'_m\) is defined as

\[
E_b = E(X_nY_m) + E(X'_nY'_m) - E(X_{n+n'}Y_{m+m'}) - E_0
\]  

(4.2)

where \(E(X_nY_m), E(X'_nY'_m), E(X_{n+n'}Y_{m+m'})\) are the potential energies of the systems containing the given clusters, and \(E_0\) is the energy of the defect-free bulk. Positive binding energies correspond here to an attraction between the defect clusters.

Figures 4.5-4.6 show the binding energies of different defect configurations as predicted by ABOP 3. The defects were added to systems of 250 bcc Fe atoms and relaxed to get the total energies needed in Equation 4.2. The binding energies for the O-V bond at different nearest neighbour (NN) separations are compared to three different DFT studies in Figure 4.5 (left). The agreement is good, ABOP 3 predicts a binding energy similar to the reference values for the most stable, the nearest neighbour O-V bond. Similar agreement is seen at longer O-V bonds, except for the second nearest neighbour (2NN) case where the binding energy is underestimated. However, the reference values for that 2NN OV defect are also fairly spread out, as opposed to the other NN distances. Figure 4.5 (right) shows the O-O binding energies at different NN distances. The energies predicted by ABOP 3 follow a similar trend as the reference DFT results, but are consistently overestimated by about 0.2–0.4 eV. The 1NN O-O configuration, i.e. two octahedral O atoms half a lattice constant away from each other, is not stable in ABOP 3 and relaxes to the (most stable) 4NN configuration (in which one lattice constant separates the O atoms). The binding energy for the 1NN case obtained by Barouh et al. is , after all, strongly negative, i.e. the interaction between the O interstitials is highly repulsive.

Figure 4.6 shows the binding energies between different \(X_2V\) configurations in iron (where \(X\) is either oxygen or vacancies) as given by ABOP 3 and compared with DFT
results by Barouh et al.\cite{Barouh2014}. The binding energies were calculated as above, using Equation 4.2 for the binding between $X$ (O or V) and OV. The exact positions of the defects are also shown in Figure 4.6. The overall agreement between ABOP 3 and the DFT results is good. For the OV$_2$ clusters (Figure 4.6, left), the binding energy for the most stable configuration is underestimated by about 0.15 eV. The other calculated energies are within the same range from the DFT values. For the O$_2$V defects (Figure 4.6, right), the binding energy for the most stable configuration is in perfect agreement with the DFT result. The other cases are within about 0.2 eV of the DFT values and follow a similar trend. Here, it is interesting to note the binding energy for the favoured case (1.6 eV) is at the same level, or even slightly higher, than the binding energy of the most stable O-V case (1NN). The presence of O$_2$V clusters in iron will therefore have a similar, reducing effect on the mobility of oxygen atoms in iron. Migrating single oxygen atoms can also easily bond to existing O-V pairs to form a O$_2$V with a similar binding energy as the original O-V pair.

Adsorption energies for oxygen atoms onto bcc iron (100) and (110) surfaces were studied with ABOP 3 and compared with published DFT results. The common adsorption sites on (100) and (110) bcc surfaces are illustrated in Figure 4.7. The
Figure 4.6: Binding energies for different OV\textsubscript{2} configurations (left) and O\textsubscript{2}V configurations (right) in bcc iron predicted by ABOP 3 and compared with DFT results \cite{5}. The binding energies are calculated as the binding between a vacancy (left) or oxygen atom (right) and an OV pair according to Equation 4.2. The illustrations of the different defect configurations are adopted from \cite{5}. Grey spheres represent Fe atoms, blue spheres oxygen, and cubes vacancies.

Figure 4.7: Common adsorption sites on a (100) bcc surface (left) and a (110) surface (right). The abbreviations marked next to each site stand for the conventional naming of the sites; on-top (T), hollow (H), bridge (B), long-bridge (LB), short-bridge (SB), and three-fold hollow (3FH).
Table 4.4: Adsorption energies and distances between the adsorbate and the top surface layer for oxygen atoms on α-Fe surfaces, calculated with ABOP 3 and compared with published DFT results. The adsorption sites are illustrated in Figure 4.7.

Adsorption energy can be defined as

\[ E_{ad} = E(\text{surface} + \text{adsorbate}) - E(\text{surface}) - E_0 \]  

where \( E(\text{surface} + \text{adsorbate}) \) is the total energy of the surface slab with the adsorbate, \( E(\text{surface}) \) the energy of the clean surface slab, and \( E_0 \) the energy of the isolated adsorbate in its ground state (in the case of ABOP 3, an oxygen molecule with \( E_{\text{coh}} = -2.583 \text{ eV/atom} \)). A more negative adsorption energy represents a stronger adsorption. The surface slabs with and without adsorbates were constructed with the relaxed Fe lattice constant of ABOP 3, and relaxed in a fixed box to keep a constant surface tension, with vacuum layers allowing the surface to relax in the surface direction and the adsorbates to move in all dimensions. Table 4.4 shows the adsorption energies predicted by ABOP 3 compared to reference values by DFT studies [19, 23, 33]. For the (100) surface, the adsorption energy of the favoured site (hollow) is in good agreement with the literature. However, the differences to the less favoured bridge and on-top sites are overestimated. This is also evident in the relaxed distances between the adsorbate and the top Fe layer, i.e. the hollow site is relaxed closer to the surface, and the bridge and on-top sites further away from the surface.
surface than the DFT values, leading to less negative adsorption energies. For the (110) surface, the strongest adsorption sites are the 3-fold-hollow and the longbridge sites. In ABOP 3, the oxygen atom relaxes towards the 3-fold-hollow site in all cases. In the On-top case, the oxygen atom moves to a position between the original site and (almost to) the 3-fold-hollow site, with an adsorption energy even slightly lower than for the 3-fold-hollow site.

For the FeO structure, the melting point and surface energies of the (100) and (110) surfaces were estimated. The melting point was determined by creating a solid-liquid interface and relaxing the system at different temperatures in NPT, \((P = 0)\) MD simulations. The melting point can be estimated as the temperature at which neither the solid or liquid phase grows. At \(T = 1350\) K the liquid phase is still quickly crystallising, but at \(T = 1450\) K the liquid phase grows. At \(T = 1400\) K, the phases are, more or less, in equilibrium for up to 100 ps, after which the liquid phase starts growing. The melting point can then be estimated to \(1400 \pm 50\) K, in reasonable agreement with the experimental value 1644 K (see Figure 4.1). It should be noted that the experimental values are for non-stoichiometric \(\text{Fe}_{1-x}\text{O}\), as perfect stoichiometric FeO does not occur in nature, and that the trend going towards stoichiometric FeO in Figure 4.1 is a decrease in the melting temperature.

The surface energies of FeO are underestimated in ABOP 3, predicting a surface energy of 25 meV/Å² for the (100) surface and 34 meV/Å² for the (110) surface compared to 61 meV/Å² and 109 meV/Å² obtained in the DFT study by Liao and Carter [32]. The surface energy, \(\gamma\), is defined as

\[
\gamma = \frac{E(\text{surface}) - E(\text{bulk})}{2A}
\]

where \(E(\text{surface})\) is the energy of the surface slab, \(E(\text{bulk})\) the energy of the bulk, and \(A\) the surface area (and \(2A\) because we have two surfaces on a slab). The surface slabs were relaxed in the same way as discussed earlier for the adsorption energies.
5 Summary

Simulating the motion of atoms requires an interatomic potential describing the interactions between the individual atoms. In this thesis, we have reviewed different types of interatomic potentials for classical atomistic simulations, such as molecular dynamics, and presented an analytical bond order potential for the Fe-O interactions.

Constructing a complete interatomic potential for the Fe-O system also requires, in addition to the Fe-O interaction, parametrisations for the Fe-Fe and O-O interactions. These single-element interactions were described by existing potentials in the analytical bond order model, and only the Fe-O interactions were parametrised in this work. Obtaining an Fe-O potential capable of describing the relative stability and structural properties of all of the most stable and common oxides (Fe$_2$O$_3$, Fe$_3$O$_4$, and FeO) proved to be difficult, if not impossible, without modifying or zeroing the pure Fe-Fe potential. The focus was therefore put on obtaining a potential with good description of oxygen defects in pure iron, while maintaining a good description of one iron oxide (FeO wüstite) and the energies of the other oxides not unreasonably far from the reference values. A good description of defect properties, such as the formation energies or binding energies of different defect structures is crucial in simulations of high-energy events such as ion irradiation. The potential was fitted against the lattice parameter, cohesive energy, and elastic properties of FeO, together with the formation energies of the octahedral, tetrahedral, and substitutional single-oxygen defect in bcc iron.

The most promising parametrisation was further tested against properties not included in the fitting database. In first principles studies, it has been shown that vacancies strongly affect the mobility and solubility of oxygen in iron. The performance of the potential for oxygen interstitials with nearby vacancies was therefore assessed. Calculations of binding energies for a number of oxygen-vacancy clusters, as well as oxygen-oxygen pairs at different interatomic separations in bcc iron, yielded an overall good agreement with first principles calculations in all studied cases. Furthermore, oxygen defects on iron surfaces were studied by calculating the adsorption energies on a (100) and a (110) surface and comparing with results from first principles calculations. The potential reproduced the order of stability of the adsorption sites for the (100) surface, while most adsorption sites on the (110) surface were unstable. For the FeO structure, surface energies and the melting point were estimated and compared with values from the literature. The potential underestimates the surface energies by a factor of two to three, while the melting point is in decent agreement with the
literature.

In conclusion, we have fitted an Fe-O analytical bond order potential capable of describing single-oxygen defects and various oxygen-vacancy clusters in bcc iron, as well as the basic properties of FeO (wüstite). The potential might be useful in high-energy or high-temperature simulations of iron with oxygen solutes, where the mobility and clustering of oxygen interstitials is important.
References


[48] Yosiko Sato and Syun-iti Akimoto. Hydrostatic compression of four corundum-type compounds: $\alpha$-Al$\text{2}$O$\text{3}$, V$\text{2}$O$\text{3}$, Cr$\text{2}$O$\text{3}$, and $\alpha$-Fe$\text{2}$O$\text{3}$. Journal of Applied Physics, 50(8):5285–5291, August 1979.


