To my husband and parents without whom I would not have been able to complete my dissertation and to my children so that they may never be afraid to chase their dreams.
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TABLE OF CONTENTS

ACKNOWLEDGMENTS ........................................................................................................ 4

LIST OF TABLES .................................................................................................................. 7

LIST OF FIGURES ................................................................................................................ 9

LIST OF ABBREVIATIONS ................................................................................................... 13

ABSTRACT .......................................................................................................................... 14

CHAPTER

1 INTRODUCTION ............................................................................................................... 16

1.1 Background .................................................................................................................... 16
1.2 Multiscale Computational Modeling .............................................................................. 17
1.3 Objectives ....................................................................................................................... 20
1.4 Outline ............................................................................................................................ 20

2 TECHNICAL DETAILS ........................................................................................................ 21

2.1 Molecular Orbital Theory .............................................................................................. 21
2.2 Ab Initio Methods .......................................................................................................... 24
    2.2.1 Hartree-Fock Theory ............................................................................................ 24
    2.2.2 Density Functional Theory ................................................................................. 25
    2.2.3 Hybrid Methods ................................................................................................... 28
    2.2.4 Geometric Optimization .................................................................................... 31
    2.2.5 Transition state Theory ...................................................................................... 34
2.3 Molecular Dynamics ...................................................................................................... 37
    2.3.1 Implementation ...................................................................................................... 38
    2.3.2 Empirical Potentials ............................................................................................ 40

3 FITTING METHODOLOGIES .............................................................................................. 46

3.1 Background .................................................................................................................... 46
3.2 Overview of Potential Development .............................................................................. 46
3.3 Building the Training Database .................................................................................... 54
3.4 Cost Functions and Precision Weighting ........................................................................ 59
3.5 Optimization Strategies ................................................................................................. 63
3.6 Testing the Parameter Set ............................................................................................. 67
3.7 When to Claim Victory .................................................................................................. 68

4 POTENTIAL OPTIMIZATION SOFTWARE FOR MATERIALS (POSMAT) ................. 70

4.1 Background .................................................................................................................... 70
4.2 Implementation and Details .......................................................................................... 71
4.2.1 Potential Optimization ........................................................................... 73
4.2.2 Cost Function ......................................................................................... 78
4.2.3 Quenching and Energy Function .......................................................... 81
4.3 Input and Output ......................................................................................... 84
  4.3.1 Parameter File ....................................................................................... 84
  4.3.2 Initialization File ................................................................................. 84
  4.3.3 Structure File ....................................................................................... 87
  4.3.4 POSMAT.out ....................................................................................... 89
4.4 MgO Buckingham Example ....................................................................... 91
4.5 Conclusions ............................................................................................... 97

5 A CHARGE OPTIMIZED MANY BODY (COMB) POTENTIAL FOR NITROGEN
CONTAINING ORGANIC MOLECULES .......................................................... 98
  5.1 Background ............................................................................................. 98
  5.2 Parameterization of COMB3 for N-OCH .................................................. 99
    5.2.1 Hydrides .......................................................................................... 108
    5.2.2 Oxides .............................................................................................. 109
    5.2.3 Cyanides ......................................................................................... 111
  5.3 Results and Discussion .......................................................................... 112
    5.3.1 Fitting Results ................................................................................. 112
    5.3.2 Energy of Adsorption on Ti/TiN Surfaces ......................................... 116
  5.4 Adsorption of Oxygen Atoms and Molecules on TiN(001) ..................... 122
  5.5 Conclusions ............................................................................................ 125

6 OXYGEN MIGRATION ACROSS TiN/TiO₂ INTERFACES ........................... 126
  6.1 Background ............................................................................................ 126
  6.2 Methods .................................................................................................. 128
  6.3 Interfacial Structures .............................................................................. 133
  6.4 Oxygen Diffusion through the Interface ................................................. 135
  6.5 Conclusions ............................................................................................ 140

7 SUMMARY OF WORK .................................................................................. 141
  7.1 General Implications ............................................................................. 141
  7.2 Future Work ............................................................................................ 142

LIST OF REFERENCES .................................................................................... 144

BIOGRAPHICAL SKETCH ............................................................................. 152
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-1</td>
<td>The Mean Approximation Error (MAE) for the atomization energy ($D_c$) and the bond lengths ($R_c$) for 39 molecules for various hybrid methods[26]</td>
<td>30</td>
</tr>
<tr>
<td>3-1</td>
<td>Comparison of properties for Cu from experiment, DFT, and COMB3.[10]</td>
<td>57</td>
</tr>
<tr>
<td>3-2</td>
<td>Heats of Formation $\Delta H$ (kcal/mol) for hydrocarbons from the second-generation REBO (REBO2), ReaxFF and COMB values are given in terms of differences from the experimental values.</td>
<td>57</td>
</tr>
<tr>
<td>3-3</td>
<td>A representative case for an even weighting scheme based on the magnitude of the property and the precision required of the property.</td>
<td>61</td>
</tr>
<tr>
<td>4-1</td>
<td>A summary of the properties currently available for targeting within POSMAT. Properties denoted with an * only for the Buckingham potential.</td>
<td>78</td>
</tr>
<tr>
<td>4-2</td>
<td>Property Values of a starting Buckingham Potential and POSMat Buckingham Potential A for MgO.</td>
<td>92</td>
</tr>
<tr>
<td>4-3</td>
<td>Property values for a starting Buckingham Potential and POSMat Buckingham fitting B for MgO.</td>
<td>94</td>
</tr>
<tr>
<td>4-4</td>
<td>Fitted Parameters developed in POSMat for the Buckingham Potential for MgO.</td>
<td>95</td>
</tr>
<tr>
<td>5-1</td>
<td>COMB3 Binary parameters for N-COH.</td>
<td>104</td>
</tr>
<tr>
<td>5-2</td>
<td>COMB3 Binary parameters for C-OH.[13]</td>
<td>105</td>
</tr>
<tr>
<td>5-3</td>
<td>COMB3 Correction parameters for Ti-N-O-C-H.</td>
<td>106</td>
</tr>
<tr>
<td>5-4</td>
<td>Summary of Target Properties and COMB3 results for Nitrogen-Hydrogen Parameterization.</td>
<td>108</td>
</tr>
<tr>
<td>5-5</td>
<td>Summary of Target Properties and COMB3 results for Nitrogen-Oxygen Parameterization.</td>
<td>110</td>
</tr>
<tr>
<td>5-6</td>
<td>Summary of Target Properties and COMB3 results for Nitrogen-Oxygen Parameterization.</td>
<td>112</td>
</tr>
<tr>
<td>5-7</td>
<td>RMS Error in the Enthalpy of Formation for various N-COH molecules.</td>
<td>114</td>
</tr>
<tr>
<td>6-1</td>
<td>Directional Stresses in fully relaxed Interfaces.</td>
<td>135</td>
</tr>
<tr>
<td>6-2</td>
<td>Energetics of fully relaxed Interfaces.</td>
<td>135</td>
</tr>
</tbody>
</table>
Summary of the work of adhesion and maximum migration energy barriers for oxygen across the interface for all stable interfaces.
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-1</td>
<td>Schematic of properties that will be investigated in this study.</td>
<td>17</td>
</tr>
<tr>
<td>1-2</td>
<td>Schematic of time and length scales and the methods used in this work.</td>
<td>18</td>
</tr>
<tr>
<td>2-1</td>
<td>Graphical representation of the energy vs. electronic interaction in order to illustrate the adiabatic connection method.</td>
<td>29</td>
</tr>
<tr>
<td>2-2</td>
<td>Illustration of three iterations of Newton's method.</td>
<td>32</td>
</tr>
<tr>
<td>2-3</td>
<td>A schematic of the minimization of a function (blue) using the conjugate gradient method (red).</td>
<td>33</td>
</tr>
<tr>
<td>2-4</td>
<td>Schematic of the possible migration paths of an atom on a surface from one free energy minimum to another.</td>
<td>35</td>
</tr>
<tr>
<td>2-5</td>
<td>The starting and final transition images used to probe the energy barrier along a migration path.</td>
<td>36</td>
</tr>
<tr>
<td>2-6</td>
<td>The Lennard Jones Potential.</td>
<td>41</td>
</tr>
<tr>
<td>3-1</td>
<td>A general fitting procedure, showing the order in which the parameter should be fit and the structures used to fit them.</td>
<td>47</td>
</tr>
<tr>
<td>3-2</td>
<td>An outline of the structures required in the training database and the order in which they should be used in the fitting.</td>
<td>56</td>
</tr>
<tr>
<td>3-3</td>
<td>Graphical Representation of downhill simplex optimization illustrating a polyhedra contracting towards the minimum in two dimensional parameter space.</td>
<td>64</td>
</tr>
<tr>
<td>4-1</td>
<td>Schematic of the flow of calculations performed in POSMat.</td>
<td>72</td>
</tr>
<tr>
<td>4-2</td>
<td>Pseudocode illustrating the allocation of the energy formalism types.</td>
<td>73</td>
</tr>
<tr>
<td>4-3</td>
<td>Pseudocode illustrating the functions required for the addition of a new optimizer using the Simplex optimizer as an example.</td>
<td>76</td>
</tr>
<tr>
<td>4-4</td>
<td>Pseudocode for a generic read_optimizer function where settings for an optimizer from the input file are read in.</td>
<td>77</td>
</tr>
<tr>
<td>4-5</td>
<td>Pseudocode for calling of specialized cost functions.</td>
<td>81</td>
</tr>
<tr>
<td>4-6</td>
<td>Sample parameter input file for COMB3 formalism in POSMat.</td>
<td>85</td>
</tr>
<tr>
<td>4-7</td>
<td>Sample of the structure portion of the input file for POSMat.</td>
<td>86</td>
</tr>
</tbody>
</table>
Parameters and Optimizer sections of the input file for POSMat

Sample structure file for an oxygen molecule in a large simulation box.

Cost detail section of a sample output file.

Structure details from a sample output file.

The minimization in error as a function of optimization step during simplex optimization A of the Buckingham Potential for MgO where point A represents the addition of targeted Pressure and B represents the addition of targeted elastic constants.

The minimization in error as a function of optimization step during simplex optimization B of the Buckingham Potential for MgO where point A represents the addition targeted elastic constants, point B the increase in weight on elastic constants.

Lattice Constant vs. Temperature for the MgO Rock Salt structure for both fitting versions from POSMat, the original Buckingham potential and experiment.

Target Energy Curve calculation for NH\textsubscript{3} illustrating the shifting of target QC values to experiment shown in the left graph as well as the targeting of bond strength (curvature) in the right graph where the COMB3 values have been shifted to match QC bond lengths in order to illustrate the error in curvature.

Charge on Nitrogen atom versus bond length for NH.

Energy versus bond length for NO and NO\textsubscript{2}.

COMB3 (abscissa) vs experimental (ordinate) values for enthalpy of formation for N-CHO molecules. The line corresponds to a perfect match between the COMB3 and experimental results.

Properties of molecules that are not described by the COMB3 N-COH Potential well.

Summary of COMB3 predicted energy per atom for hypothetical N-COH solid phases as compared to DFT calculations.

The structures used to calculate the energy of adsorption.

Adsorbant sites denoted A-F(yellow) for the Ti(0001) [left] and the TiN(001) [right] where Ti atoms are grey and Nitrogen atoms are blue.

Summary of the binding energies for selected geometries as compared to DFT calculations. Values are color-coded to represent the type of adsorption;
The Comparison of binding energies for NO2 on both Ti and TiN surfaces based on differing correction term fits. The values are color coded to represent the types of physics present for each case; pink represent non-adsorbed molecules, yellow represent physisorbed molecules and green represent chemisorbed molecules.

Summary of the binding energies for all molecules tested in COMB3 for all Adsorption Sites.

Snapshots from MD simulations following the deposition of 60 oxygen atoms deposited on TiN (001), where grey represents Ti atoms, blue represents nitrogen atoms, and red represents oxygen atoms.

Snapshots from MD simulations following the deposition of O2 on TiN (001). The atoms are color coded by atomic charge with the values indicated by the color bar.

Schematic of the cross section of the oxide scale structure on TiN.

Relaxed TiO2 and TiN surfaces used to construct the interfaces the TiN/Oxide Interfaces; Ti (Light Blue), Oxygen (Red), Nitrogen (Purple).

Schematic of the oxygen diffusion path to be investigated for the TiN(001) Interfaces where the large blue atoms are Ti, the small purple atoms are Nitrogen and the red atom is oxygen.

Schematic of the oxygen diffusion path to be investigated for the TiN(111) Interfaces where the large blue atoms are Ti, the small purple atoms are Nitrogen and the red atom is oxygen.
6-10 Geometric Relaxation of an NEB image. .............................................................. 137
6-11 Energy barrier for oxygen migration across all three interfaces....................... 139
# LIST OF ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>COMB3</td>
<td>Charge Optimized Many Body Potential</td>
</tr>
<tr>
<td>DFT</td>
<td>Density Functional Theory</td>
</tr>
<tr>
<td>GGA</td>
<td>Generalized Gradient Approximation Local Density Approximation</td>
</tr>
<tr>
<td>LAMMPS</td>
<td>Large-Scale Atomic/Molecular Massively Parallel Simulation</td>
</tr>
<tr>
<td>LDA</td>
<td>Local Density Approximation</td>
</tr>
<tr>
<td>NEB</td>
<td>Nudged Elastic Band</td>
</tr>
<tr>
<td>MD</td>
<td>Molecular Dynamics</td>
</tr>
<tr>
<td>QC</td>
<td>Quantum Chemical</td>
</tr>
<tr>
<td>VASP</td>
<td>Vienna Ab Initio Simulation Package</td>
</tr>
</tbody>
</table>
The use of Molecular Dynamics (MD) in materials simulation offers a powerful tool for the investigation of materials on a nanometer to micron length scale and allows for the study of complex defect structures under dynamical conditions. However, the reliability of MD depends heavily on the choice of energy formalism and the subsequent material potential used. While the number of potentials available for the wide array of energy formalisms is vast, there is little literature addressing how these potentials were created and how to best begin the development of a new potential. This work attempts to address this problem by presenting a systematic methodology for potential development, including methods and recommendations for training set creation and targeting specific properties with differing parameters in the formalism. This work also presents POSMat (Potential Optimization Software for Materials), a software specifically developed to facilitate the fitting process. POSMat offers a variety of optimization algorithms, formalisms, and targetable properties in a parallel programming framework which can calculate properties quickly and efficiently.
This work then uses these tools and methodologies to develop third-generation Charge Optimized Many Body (COMB3) potentials for N-H, N-O, and N-C systems (N-COH). These potentials fill a gap within the COMB3 framework and, when combined with existing potentials, allow the investigation of the oxidation behavior of TiN systems. These potentials were developed by targeting the energetic and geometric properties of small molecules and were then tested against a larger set of molecules. To test the applicability to the oxidation behavior of TiN systems, the adsorption energies were calculated for a subset of test molecules on Ti(0001) and TiN(001) surfaces and were compared to predictions of Density Functional Theory (DFT). Dynamical simulations were then conducted by depositing oxygen atoms and molecules on a TiN surface; the results were compared to the known oxidation behaviors of TiN.

DFT was used to investigate into the protective nature of oxide scales in TiN systems. Differing terminations of TiN were paired with multiple TiO$_2$ phases and terminations and the energy of adhesion was calculated in order to determine the most stable interface structures. In order to study the likelihood of continued oxide growth at the interfaces, the energy barriers for oxygen diffusion across the interfaces were determined.
CHAPTER 1
INTRODUCTION

1.1 Background

Titanium nitride (TiN), a material system known for its high hardness, wear-resistance, corrosion resistance and extremely high melting temperature, has found widespread use in a variety of applications such as in cutting tools, turbines, and as the protective heat shield for the space shuttle[1]. These applications are often at elevated temperatures and in oxygen rich environments. These conditions favor the formation of oxide scales which lack the desirable properties of the base material. Therefore, understanding the oxidation, defect and surface properties of TiN is of major importance. Although oxidation is a spontaneous process and cannot be prevented for many metallic and intermetallic systems, in some cases it can be controlled. A protective oxide scale acts as a diffusion barrier and prevents further corrosive attack which is more desirable than unmitigated growth of a non-protective oxide scale[2]. Many studies have attempted to increase the oxidation resistance or to increase the likelihood of the creation of a protective, rather than non-protective, oxide scale for TiN using alloying and surface modifications. Alloying TiN with varying elements including aluminum, zirconium, carbon, and vanadium has led to varying degrees of increased oxidation resistance[3, 4]. Examples of attempts to improve the oxidation resistance through surface modifications include thermal spraying, plasma spraying, ion plating, sputtering, and ion implantation [5, 6]. Such modifications can also lead to varying degrees of improvement in other desirable properties.
1.2 Multiscale Computational Modeling

In many cases, the interfacial structures present in heterogeneous materials can be difficult to probe experimentally. Therefore, computational modeling can be extremely helpful in understanding the physics and chemistry effects present in these structures at an atomistic and electronic level. Any single method used to investigate these systems can only illuminate physical and chemical properties at a small range of time and length scales. Using multiple modeling techniques in tandem allows for the bridging of time and length scales in order to create a full and realistic explanation of the materials processes present, as shown in Figure 1-2.
The use of multiple modeling techniques requires the development of a consistent theoretical approach, which seamlessly transitions from electronic structure based methods to atomistic methods. The utilization of multiple techniques, in order to validate the modeling predictions, is necessary. In this work both *ab initio* methods, such as hybrid methods, Density Functional Theory (DFT) and Molecular Dynamics (MD) simulations are used in order to bridge the time and length scales.

*Ab initio* methods at the level of DFT can be used to study the physical and electronic properties of the bulk systems and point defects. DFT will be used to probe the properties of TiN/TiO₂ interfaces, as will be seen in subsequent sections. However, due to geometrical constraints and the mechanical properties inherent in these material
systems, only a small subset of interfaces can be investigated using this method. MD methods can simulate larger system sizes, enabling the investigation of a larger array of structures.

MD requires the use of empirical potentials (mathematical expressions) which model the energy and forces of a system. For a heterogeneous system, the empirical potential used, by necessity, must be able to model a wide array of bonding types and environments. Reactive force field potentials such as REBO, ReaxFF and COMB3 offer the flexibility and robustness to describe dynamical processes of multi-component systems. However, in order to use any of these formalisms, potentials would need to be developed. While Reactive Empirical Bond Order (REBO) potential[7] does an exceptionally good job in modeling organics, little work has been done to include metal oxides and intermetallics, and to the best of the author’s knowledge, there are no published potentials available for this class of material. ReaxFF (‘Reactive Force Field’) [8] describes both nitrogen-containing organic molecules and Titanium Dioxide (TiO₂), but the two potentials are not compatible having differing oxygen parameters. ReaxFF is also missing the necessary TiN parameters. The third-generation Charge Optimized Many Body (COMB3) potential[9-13] is the most complete having binary parameter sets for TiN, TiH, TiO, TiC, CO, CH, and OH systems. The only potentials where development is necessary are for the NC, NO and NH (N-COH) systems.

Potential development is an extremely complex undertaking. There are few tools and information available for the development of empirical potentials. A rigorous methodology for the development of potentials is required. Most programs used for potential development are created by the potential developer or are in house codes
used by multiple people within a single research group. In these cases, the
development code is often untested and unrefined. Thus, systematic and tested tools
are needed for the development of empirical potentials.

1.3 Objectives

The objectives of this dissertation are:

1. To present a systematic approach for empirical potential development and to
develop the tools necessary to quickly and efficiently develop empirical
interatomic potentials that have high materials fidelity.

2. To develop a Charge Optimized Many Body (COMB3) potential for N-COH
systems to fit within, and be consistent within, the previously developed
potentials so that it can be used to investigate oxidation behavior in metal-nitrides
and carbides.

3. To understand the oxidation behavior and stability of fully formed TiN/Oxide
Interfaces utilizing DFT methods.

1.4 Outline

The dissertation is organized as follows. It begins by detailing the computational
methods in Chapter 2. It follows with a methodology for the development of empirical
potentials in Chapter 3. In Chapter 4, a simulation code that facilitates the development
of empirical potentials is presented. Chapter 5 presents a COMB3 N-COH potential
using the methods and code presented in the previous chapters. Chapter 6 then
continues the work to investigate the oxidation behavior of TiN utilizing DFT. Finally,
Chapter 7 presents conclusions and perspectives for future work.
CHAPTER 2
TECHNICAL DETAILS

Computational simulations are frequently used to study a wide range of properties for heterogeneous systems. This current study employs electronic structure calculations at the level of DFT and so-called Hybrid Methods, and atomistic simulations utilizing MD. The following sections discuss the relevant aspects of these methods.

2.1 Molecular Orbital Theory

Quantum Chemical (QC) methods can provide the most accurate energy calculations available. Advanced QC methods are the most expensive, and are generally reserved for small system sizes such as molecules and small clusters. QC methods are derived from the many electron, time independent Schrodinger Equation given in Eq. (2-1)[14].

\[ \hat{H}\psi = E\psi \]  

(2-1)

In the above equation, E is the energy eigenvalue, \( \psi \) is the wave function (i.e., the eigenvector corresponding to the particular eigenvalue) and \( \hat{H} \) is the Hamiltonian operator. The wave function itself is not an observable quantity, but the square of the wave function is interpreted as the probability of finding an electron within a given volume at a particular point in space. Each eigenfunction, \( \psi \), is associated with its own energy eigenvalue \( E_i \). The lowest energy states are generally the most relevant because electrons in the groundstate are added from the lowest energy upwards. For a very limited number of cases, such as a harmonic oscillator or a hydrogen atom, the Schrodinger equation can be solved exactly and analytically, yielding the eigenvalues and eigenvectors. For nearly all systems, however, the Schrodinger Equation cannot be solved exactly, and approximate solutions have to be determined.[14-16] A number of
estimated wave functions have been constructed and are referred to as basis sets. The basis set is a set of functions that represent the physical space where an electron can be found such as, but not limited to, the atomic orbitals, valence orbitals, plane waves in a material or real space.

The Hamiltonian is used to describe the energy of the system; for a system consisting of atoms (electrons and nuclei) the Hamiltonian is given as the sum of the kinetic energy ($\hat{T}$), the electrostatic interaction between electrons and nuclei ($\hat{U}$), the repulsion between electrons ($\hat{R}_e$), and the repulsion between nuclei ($\hat{R}_n$) and is given as:

$$\hat{H} = [\hat{T} + \hat{U} + \hat{R}_e + \hat{R}_n]$$

$$= \left[ -\sum_i^N \left( \frac{\hbar^2}{2m_i} \nabla_i^2 \right) - \sum_k^N \left( \frac{\hbar^2}{2m_k} \nabla_k^2 \right) \right]$$

$$- \left( \sum_i^N \sum_k^N \frac{e^2Z_k}{r_{ik}} \right) + \left( \sum_{i<j}^N \frac{e^2}{r_{ij}} \right) + \left( \sum_{k<l}^N \frac{e^2Z_kZ_l}{r_{kl}} \right)$$

where $i$ and $j$ run over electrons, $k$ and $l$ run over the nuclei; $\hbar$ is Plank’s constant divided by $2\pi$, $m$ is the mass of the particle, $e$ is the charge, $Z$ is the atomic number and $r$ is the distance between particles.[14-16]

In this general form, the equation is impossible to solve due to the interdependence of terms within the Hamiltonian. The properties of each particle in the system (such as position, energy or velocity), are dependent on the properties of all of the other particles in the system. This phenomenon is known as ‘exchange’ and ‘correlation’. Exchange refers to the quantum mechanical effect experienced between identical particles with the same spin. Electrons are Fermions and no two electrons can have the same quantum numbers. Therefore, when two electrons exchange places, the
sign of the eigenfunction must change, a principle known as antisymmetry. Correlation refers to the energy dependence of electrons on each other, specifically electrons repel each other and there is an energy associated with these dispersion forces.[14-16]

The Born-Oppenheimer approximation is used to separate the atomic and electronic degrees of freedom; it states that during an electronic relaxation, the motion of nuclei are much slower than that of the electrons [17] so that the two interactions may be separated. The positions of the nuclei are assumed to be, relatively speaking, fixed so that the kinetic energy of the nuclei may be calculated separately from the kinetic energy of the electrons. However, this approximation does not account for the electron-electron correlation or the exchange energy which still must be taken into account. [14-17]

The Hamiltonian in the Schrodinger Equation may only be explicitly solved for systems simpler than H$_2^+$, due to the electron-electron correlation and exchange. In the case of H$_2^+$, there is only one electron in the system so electron-electron interactions are absent. However, for any system containing more than one electron further assumptions must be made.

The simplest approximation is to simply ignore electron-electron correlation and exchange. In this case, the wavefunction can be considered a combination of one electron wavefunctions. The Hartree product states that the total wavefunction, $\Phi$, is a product of one electron wavefunctions shown in Eq. (2-3).

$$\Phi(x_1, ..., x_N) = \psi_{j_1}(x_1) \ast \psi_{j_2}(x_2) \ast \ldots \ast \psi_{j_N}(x_N) \quad \text{(2-3)}$$

Although the Hartree product is fundamentally flawed as it does not take into account exchange or correlation, it is the logical first step in describing a many electron
system. The types of assumptions made for the correlation and exchange energy determine the different classes of QC methods and implementations of molecular orbital theory, which will be discussed further in the subsequent section. [14, 18]

2.2 Ab Initio Methods

Ab Initio methods, Latin for ‘from the beginning’, are computational chemical methods that are based on quantum chemistry.

2.2.1 Hartree-Fock Theory

An approach for dealing with the issue of exchange is to combine the one electron wavefunctions in an appropriate manner, which the Hartree Approximation doesn’t do. Instead of forming the wavefunction from a simple product of one-electron wavefunctions, a Slater determinant may be used. This construction imposes the antisymmetry of the overall wavefunction, which is fundamental to exchange. For a two electron system, the Slater determinant is given as

\[
\Phi(x_1, x_2) = \frac{1}{\sqrt{2}} \det \begin{bmatrix} \psi_j(x_1) & \psi_j(x_2) \\ \psi_k(x_1) & \psi_k(x_1) \end{bmatrix}
\]

\[
= \frac{1}{\sqrt{2}} \left[ \psi_j(x_1)\psi_k(x_1) - \psi_j(x_2)\psi_k(x_1) \right]
\] (2-4)

A simple approach for dealing with the correlation is for each electron to see all the other electrons as an average field. Electron-electron attraction is thus accounted for in an averaged way. However, the repulsion-repulsion term must still be accounted for, which can be done by integrating over the charge density (probability). The interaction potential \(\hat{R}_e\) previously seen in Eq. (2-2), accounts for this correlation between electron \(i\) and \(j\) and can be described as:
\[ \hat{R}_e = \sum_{i \neq j} \int \frac{\rho_j}{r_{ij}} d\mathbf{r} \]  

(2-5)

where \(\rho_j\) is the charge density of electron \(j\) and \(r_{ij}\) is the distance between atom \(i\) and \(j\).

However, the density is not explicitly known. An iterative method to solve this problem, called The Self-Consistent Field Method, was proposed by Hartree[19]. The first step involves an initial guess for the charge density. From this, the necessary one electron Hamiltonians may be constructed and the differential equation solved. From this, a new density may be calculated from the improved wave function. This new density may then be used to repeat the process self-consistently until the change in the energy and electron density are small enough to meet a predetermined tolerance.[14-16]

While the inability to determine the exact correlation can have a drastic impact on the ability to construct accurate wave functions, Hartree-Fock theory was able to for the first time carry out practical molecular orbital calculations. Subsequent \textit{ab initio} methods attempt to build on the foundation of Hartree-Fock theory while endeavoring to better account for the exchange-correlation energy.

\subsection*{2.2.2 Density Functional Theory}

Hartree-Fock is an N-body problem that becomes increasingly more computationally expensive as the system size increases. DFT attempts to resolve the computational load concern by replacing the unknown point charge electron densities with an observable charge density. While early attempts at constructing a Hamiltonian from a charge density functional found some initial success[20-22], the methods lacked a rigorous theoretical foundation and so went largely unused until the theorems of Hohenberg and Kohn.
The Hohenberg-Kohn Existence Theorem states, “The external potential $v_{\text{ext}}(r)$, and hence the total energy, is a unique functional of the electron density $n(r)$”[23]. The proof proceeds by *reductio ad absurdum*. It starts with an assumption that two different external potentials will result with the same electron density. The external potentials are associated with their own Hamiltonians and therefore their own unique groundstate energies. Applying the variational principle yields a contradiction where the sum of both groundstates is less than the sum of the groundstates. Therefore the assumption is false.[23]

While this theorem proves that if the correct charge density is known, the groundstate properties of a system may be calculated, it does not help in identifying what the correct charge density actually is. The Hohenberg-Kohn Variational Theorem addresses this problem and states, “The groundstate energy can be obtained variationally: the density that minimizes the total energy is the exact groundstate density.”[23] The proof states that if the density $n(r)$ is known, then the external potential, $V_{\text{ext}}(r)$, is known. The number of electrons in the system and the external potential determine the Hamiltonian and therefore the wavefunction, which ultimately means that the wavefunction is a functional of the electron density. By applying the variational principle, electron densities can be compared by the groundstate energies that result from them. Therefore, in practice, one may use an iterative process where the density may be slowly improved using decreasing energy as a metric. However, there is still no guarantee that the system will have the true lowest energy state because the density functional chosen may not be powerful enough to do this.[23]
While the previous theorems offered promise for the prospects of DFT, they did not help in identifying the actual functional for the charge density. The Kohn-Sham Equations builds on the previous work by offering a functional form for the density. The key assumption is the mean field approximation, which states that the energy due to non-interacting electrons in the Schrödinger Equation can be replaced by an effective potential energy ($V_{\text{eff}}$) where the effective potential energy is dependent on the electron density. This results in a simplification of the many body Hamiltonian that cannot be solved exactly to a sum of single particle Hamiltonians which can be solved given in Eqs. (2-6) and (2-7)[24].

\[
\left[-\frac{\hbar^2}{2m_i} \nabla_i^2 + V_{\text{eff}}(r)\right] \psi_i(r) = E \psi_i(r) \tag{2-6}
\]

\[V_{\text{eff}}(r) = V_{\text{ext}}(r) + V_{\text{Hartree}}(r) + V_{\text{xc}}(r) \tag{2-7}\]

$V_{\text{Hartree}}$ is the Hartree potential and represents the Coloumbic repulsion between an electron and the remaining electron density ($n(r)$) and is shown in Eqs (2-8) and (2-9).

\[V_{\text{Hartree}}(r) = e^2 \int \frac{n(r')}{|r-r'|} d^3r' \tag{2-8}\]

\[n(r) = \sum_i \psi_i^*(r)\psi_i(r) \tag{2-9}\]

$V_{\text{ext}}$ is the external energy, and must be chosen so that the resulting electron density is the same as the groundstate density. As previously suggested by the variational theorem, an iterative approach is utilized, in which a charge density is chosen in order to calculate $V_{\text{ext}}$ and is then used to solve the Kohn-Sham equations. This results in a new electron density. At this point if the new charge density is the same
as the charge density in the previous iteration (to some prescribed tolerance) then the equations are deemed to be self-consistent and the energy as well as other properties may by calculated. If they are not yet self-consistent then the process is repeated until the electron densities converge.[15, 16]

$V_{xc}$ is the exchange-correlation energy and represents the energy from the interaction of each electron with all the other electrons in the system, which cannot be solved explicitly, except for a gas of free electrons. A number of approximations for the exchange-correlation energy have been developed, the most common of which is the local-density approximation (LDA). In LDA, it is assumed that the charge density in any spatial location is the same as the charge density for a homogenous free gas electron system of the same density. It is also assumed that only the density where the functional is being evaluated is of importance. In spite of these assumptions, LDA performs remarkably well for many systems. Two drawbacks to LDA are that the binding energies are often overestimated which results in an underestimation in cell parameters, and insulating systems with strong correlation effects are often predicted to be metallic[16].

The generalized gradient approximation (GGA) improves upon LDA by introducing a dependence on the gradient of the electron density at the coordinate that the functional is being calculated. GGA tends to correct the over binding displayed by LDA in most systems but does not correct the incorrect band gap predictions in strongly correlated insulating systems[25].

**2.2.3 Hybrid Methods**

Additional enhancements in the exchange correlation energy came with the Adiabatic Connection Method which reintegrates the Hartree exchange energy
mentioned in the previous section to create hybrid functionals. This method imagines a variable \( \lambda \) which describes the amount of electron interaction. The interaction ranges from 0 (no interaction) to 1 (exact interaction). For such a system, the exchange correlation energy is therefore the integral of the groundstate energy as a function of the interaction function, or the area under curve shown in Figure 2-1.[15]

![Graphical representation of the energy vs. electronic interaction](image)

Figure 2-1. Graphical representation of the energy vs. electronic interaction in order to illustrate the adiabatic connection method.

The left most point on the curve corresponds to a non-interacting system and could be taken as the Hartree Fock energy discussed in the previous section. While the right most point, corresponding to an accurately correlated system, is unknown, the exchange correlation energy calculated from DFT is a reasonable approximation. The simplest approximation for the area can be represented as the area of rectangle A and a fraction (z) of rectangle B given in Eq. (2-10).

\[
E_{xc} = E_{xc}^{HF} + z(E_{xc}^{DFT} - E_{xc}^{HF})
\] (2-10)
The parameter $z$ can then be treated as being optimizable to yield the highest fidelity materials properties. More complicated functionals have been developed using additional tunable parameters. For example, for the B3LYP method the functional is shown in Eq. (2-11).

$$E_{xc}^{B3LYP} = E_x^{LDA} + 0.20(E_x^{HF} - E_x^{LDA}) + 0.72(E_x^{GGA} - E_x^{LDA})$$

$$+ 0.81(E_c^{GGA} - E_c^{LDA})$$

Such methods are computationally more expensive than DFT alone due to the inclusion of the Hartree-Fock energy; however, they have been found to be more accurate. A comparison of the relative accuracy of common hybrid methods is shown in Table 2-1. As can be seen, B3LYP and B3tLap have the highest accuracies in both energies and geometries. While B3tLap is more accurate in terms of energy, B3LYP predicts the geometries the best out of the hybrid methods presented here.[15]

<table>
<thead>
<tr>
<th>Method</th>
<th>MAE for $D_c$ (kcal/mol)</th>
<th>MAE for $R_c$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Diatomic</td>
<td>Polyatomic</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>XC with</td>
<td>no HF exchange</td>
<td></td>
</tr>
<tr>
<td>BLYP</td>
<td>5.58</td>
<td>5.23</td>
</tr>
<tr>
<td>Blap3</td>
<td>3.30</td>
<td>8.39</td>
</tr>
<tr>
<td>BtLap</td>
<td>3.08</td>
<td>3.81</td>
</tr>
<tr>
<td>XC with</td>
<td>HF exchange</td>
<td></td>
</tr>
<tr>
<td>BMK</td>
<td>2.72</td>
<td>2.49</td>
</tr>
<tr>
<td>M06</td>
<td>2.69</td>
<td>2.57</td>
</tr>
<tr>
<td>B3LYP</td>
<td>2.51</td>
<td>1.82</td>
</tr>
<tr>
<td>B3tLap</td>
<td>2.04</td>
<td>2.13</td>
</tr>
</tbody>
</table>
2.2.4 Geometric Optimization

To this point, the nuclei have been treated as being fixed in space, with the energy calculated through an iterative estimation of the electron density, which is also known as electronic relaxation. However, to find the true minimum energy of a structure, the nuclei must also be allowed to move to their low energy positions; this is termed geometric optimization. A multi-atom system offers an energy minimization problem with multiple degrees of freedom; i.e. each atom has the ability to change position within three-dimensional space. This becomes a numerical optimization problem; there are a number of methods for solving this type of challenge, each with its advantages and disadvantages.[16, 27]

Newton’s method is one approach that may be utilized. For clarity, this method will be described in one dimension; it can be easily expanded into three dimensions. In order to find the local minimum of the energy function, \( f(x) \), one can simply find the value of \( x \) where \( df/dx = 0 \), denoted \( x^* \) and check that this defines a minimum instead of a maximum. Newton’s method then defines the derivative of \( f(x) \) as \( g(x) \) and uses the Taylor expansion to calculate the tangent to \( g(x) \) at an initial guess \( (x_1) \) as shown in Figure 2-2. This tangent at \( x_1 \) is then used to find the first estimate of the point where \( g(x) = 0 \). This new value of \( x^* \) is used to calculate the tangent and a new estimate for \( x^* \) until a predefined convergence criteria is met.[16, 27]

Newton’s method can be extended to three dimensions by replacing the Taylor expansion with a \( 3N \times 3N \) matrix of partial derivatives of the function \( g(x,y,z) \). Notice that the elements of this matrix are in fact second partial derivatives of the desired energy function \( f(x,y,z) \). While Newton’s method converges quickly in three dimensions, it requires the calculation of the second derivative. When the basis set is based on plane
waves, this calculation is not only computationally expensive but impractical. Quasi-
Newton methods replace the $3N \times 3N$ matrix with an approximation that is updated
iteratively. However, each new iteration is not based on the current iteration alone, but
also the previous iterations. This means that convergence process cannot begin until
four or five iterations have been performed.[16, 27]

Figure 2-2. Illustration of three iterations of Newton's method.

Another approach to geometrical optimization is the conjugate gradient method
which is based on the steepest descent method. The steepest descent method simply
moves from point $P_i$ to point $P_{i+1}$ as many times as needed along the local downhill
gradient until the local gradient is zero. Because the steepest descents method has a
stopping criterion based solely on the gradient being zero, it can often stop at false
minima such as saddle points. The conjugate gradient method will be presented using
the problem of a minimization of a 2-dimensional function. In order to minimize the
function \( E(x) \), given a starting point, \( x_0 \), it is logical to look along the path where the function decreases the most rapidly. From vector calculus, this can be defined as the negative of the gradient of the function at \( x_0 \). The function can then be iteratively minimized by moving \( x \) by the gradient of the function multiplied by a suitable step size. The optimal step size would be the one that minimizes \( E(x) \) more than any other step size. The gradient at the new location \( x_1 \) can now be calculated and if the optimal step size was chosen it can be shown that the new search direction and the one from the previous step are orthogonal. However, the optimal step size is often unknown and the current and previous search directions will not be orthogonal. The conjugate gradient method, however, insists that the search directions be orthogonal. Therefore, the new search direction must undergo orthogonalization, in which the portion of the new vector that can be projected along the previous search direction is removed. A schematic of the conjugate gradient method (red) can be seen in Figure 2-3.[16, 27]

Figure 2-3. A schematic of the minimization of a function (blue) using the conjugate gradient method (red).
The methods stated above are two of the most widely used for generic DFT geometry optimizations due to their efficiency. No matter which method is used, when applied to a multi-atomic system, a new electronic optimization must be performed before each geometric optimization step, due to the change in electron densities from the movement of nuclei. The system is considered to have converged when the magnitude of all of the forces are less than a given convergence criteria.

While each atom may be experiencing forces larger than a given convergence criteria, due to Newton’s Third Law the forces will pull in opposite directions balancing the entire force of the system. This presents a particular problem when optimizing highly symmetric structures. For the optimization of a linear molecule (i.e. bond angle equal to 180°), due to symmetry, the total forces will cancel and while the bond lengths may vary during the optimization, the bond angle will not due to the constraints of the initial guess in the geometry. It can be seen in these types of cases that the stresses may be non-zero indicating that a groundstate has not been found. These symmetry problems can be overcome by purposefully breaking the symmetry for the initial guess of the structure.[16, 27]

2.2.5 Transition state Theory

There are many physical and chemical processes where the rate of the process is important, such as oxygen diffusion during oxidation. Atomic-level simulation offers a useful tool in evaluating such processes using transition state theory. On a surface, there may be many low energy sites for an adatom to sit on, separated by high energy barriers. According to transition state theory, the rate of a given process (k_{A->B}), such as the diffusion of an adatom from one low energy site to another, is directionally related to the energy required to overcome the energy barrier (\Delta E) as shown in Eq. (2-12).[16]
\[ k_{A \rightarrow B} = \nu \exp \left( -\frac{\Delta E}{k_B T} \right) \]  

(2-12)

In the above equation, \( \nu \) is the vibrational frequency of the atom in the potential minimum, \( k_B \) is Boltzmann’s constant, and \( T \) is the temperature in Kelvin. As shown in Figure 2-4, there may be a number of migration paths from one energy minimum to another. Finding the most likely path with the highest rate from Eq. (2-12) means finding the migration path with the lowest energy barrier. Using DFT to calculate the barriers of the differing paths becomes difficult when, as stated in the previous section, the adatom relaxes back to the low energy structure.[16]

Figure 2-4. Schematic of the possible migration paths of an atom on a surface from one free energy minimum to another.
Elastic band theory is a simple method for finding the minimum energy path. In this method, the structures or transition images along the path should use the lowest amount of energy and be evenly spaced between the beginning and ending low energy structures which are held as fixed points, as shown in Figure 2-5. The minimum energy path \( M \) is a function of each image \( r_i \) and is defined as

\[
M(r_1, r_2, ..., r_f) = \sum_{i=1}^{f-1} E(r_i) + \sum_{i=1}^{f} \frac{K}{2} (r_i - r_{i-1})^2
\]  

(2-13)

where \( E(r_i) \) is the total energy of the \( i \)th image and \( K \) is the spring stiffness connecting adjacent images.[16]

Figure 2-5. The starting and final transition images used to probe the energy barrier along a migration path.
The elastic band method does have its drawbacks. If the stiffness constant is too low, the images tend to slide downhill away from the energy barrier resulting in an underestimation of the energy barrier. Another problem is known as “corner cutting” and occurs when a path is found that minimizes Eq. (2-13) but does not locate the true transition state due to curvature in the path.[16]

The Nudged Elastic Band (NEB) method[28], which is used in this work, looks to improve on the elastic band method by minimizing forces instead of energy. There are two forces included in the minimization. The real forces, those which result from the potential energy, act perpendicular to the path. Artificial spring forces act parallel to the path, keeping the images connected as they move toward the minimum energy path. The NEB method is an iterative method and converges when the sum of the forces is equal to the forces of the springs. The rate of convergence is dependent on the initial guess of the path. It should also be noted that the description of the minimum energy path improves as more images are included. However, the calculation becomes more computationally expensive as more images are included. [16]

2.3 Molecular Dynamics

While DFT has proven to be successful in describing many materials systems, due to the high computational cost it is limited to small system sizes: usually less than 1000 atoms. However, linear scaling DFT[29] can calculate systems sizes larger than this if enough computational resources are available. Atomistic simulations offer an alternative to DFT for applications requiring larger system sizes because they are computationally much cheaper. Instead of modeling each electron present in the system as in DFT, atomistic simulations represent the effect of the electrons on the interatomic interactions through an empirical potential, or energy formalism. With this formalism,
one can either perform a static energy minimization or evolve the system in time through the integration of Newton’s equation of motion in an MD simulation.[30]

2.3.1 Implementation

A static energy minimization can be conducted through the small movements of atoms within a structure until the energy is minimized. This can be done in a number of different ways, including steepest descent[31], the Hessian-free truncated Newton algorithm[32] and conjugate gradient methods[32] mentioned in Section 2.2.4.

The system may also be allowed to dynamically evolve by integrating Newton’s equations of motion. One such method for reliably integrating Newton’s equations of motion with little error is the Verlet algorithm.[33] Newton’s equation of motion is given in Eq.(2-14), where F is the force on an atom, m is the mass of an atom and \( \frac{d^2x(t)}{dt^2} \) is the second time derivative of atomic position or the acceleration. In one-dimensional space, the force can be written as the derivative of the potential energy U as shown in Eq. (2-15). In this case the force is a function of the coordinate of the atom.

\[
F = m \frac{d^2x(t)}{dt^2} \quad (2-14)
\]
\[
F = -\frac{dU}{dx} \quad (2-15)
\]

The problem then reduces to an accurate description of the potential energy and solving the second order differential equation for the motion of particles. The first part of the problem will be discussed in greater detail in subsequent sections. In order to solve the second aspect of the problem, we start by assuming that time evolves in discrete steps i.e. time steps given as \( \Delta t \). Using the Taylor Expansion to expand by the time step around the position \( x(t) \) yields Eq. (2-16) and Eq. (2-17).
\[
x(t + \Delta t) = x(t) + \Delta t \frac{dx(t)}{dt} + \frac{\Delta t^2}{2} \frac{d^2x(t)}{dt^2} + \frac{\Delta t^3}{3} \frac{d^3x(t)}{dt^3} + O(\Delta t^4)
\]

\[
x(t - \Delta t) = x(t) - \Delta t \frac{dx(t)}{dt} + \frac{\Delta t^2}{2} \frac{d^2x(t)}{dt^2} - \frac{\Delta t^3}{3} \frac{d^3x(t)}{dt^3} + O(\Delta t^4)
\]

By adding Eq. (2-16) and Eq. (2-17) the odd terms cancel, resulting in the Verlet algorithm for position shown in Eq. (2-18). The fourth order and higher terms are neglected and the error associated with this negation is stable and decreases rather than increases as time progresses.

\[
x(t + \Delta t) = 2x(t) - x(t - \Delta t) + \frac{\Delta t^2 F(x(t))}{m} + O(\Delta t^4)
\]

The velocity Verlet Algorithm is derived in the same way wherein the Taylor expansion is used to expand around the velocity \(v(t)\) shown in Eq. (2-19).

\[
v(t + \Delta t) = v(t) + \Delta t \frac{dv(t)}{dt} + \frac{\Delta t^2}{2} \frac{d^2v(t)}{dt^2} + O(\Delta t^3)
\]

Newton's Second Law, Eq. (2-14), can be used to replace \(dv/dt\) (acceleration) with \(F/m\). An expression for the second derivative of velocity can be found by using the Taylor Expansion to expand around \(dv/dt\) by \(\Delta t\) as shown in Eq. (2-20).

\[
\frac{dv}{dt}(t + \Delta t) = \frac{dv(t)}{dt} + \Delta t \frac{d^2v(t)}{dt^2} + O(\Delta t^2)
\]

Multiplying Eq. (2-20) by \(\Delta t/2\) and rearranging the equation yields an expression that may be substituted for the second derivative of the velocity in Eq. (2-19). The velocity Verlet algorithm is then given in Eq. (2-21).

\[
v(t + \Delta t) = v(t) + \frac{\Delta t}{2m} \left( F(x(t + \Delta t)) + F(x(t)) \right) + O(\Delta t^3)
\]
2.3.2 Empirical Potentials

Over the last few decades, a large number of interatomic potentials have been developed to describe various bonding types and environments. To take representative examples, the Lennard-Jones potential was developed for van der Waals interactions[34], the Embedded-Atom Method (EAM) potential for metallic systems[35], the Buckingham potentials for ionic systems[36], the Assisted Model Building with Energy Refinement (AMBER) force fields for biomolecules[37], and the Tersoff potential for covalently bonded materials[38]. While each of these methods is capable of describing the class of materials for which it was designed, none can describe the multiplicity of bonding and chemical environments present in many complex materials structures such as interfaces. Interfaces between dissimilar material types are used in a diverse range of applications, such as corrosion/oxidation, pn junctions in semiconductor devices, and polymer matrix composites. The imperative for this capability led to extensions of some of the previously mentioned formalisms, such as MEAM[39], and the development of reactive interatomic potentials, such as the REBO potential[7], the Charge Optimized Many Body (COMB3) potential[13, 40-42] potential and ReaxFF[8] potential. The potentials used in this work are discussed in greater detail in subsequent sections.

2.3.2.1 Lennard-Jones Potential

The Lennard-Jones potentials was one of the first descriptions of interatomic interactions[34] and describes the interatomic interaction between two charge neutral charged atoms. In practical terms, the interatomic interaction can be viewed as the sum of the attractive and repulsive energy and is given as
$$U_{LJ} = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right]$$

(2-22)

where the energy is $U_{LJ}$, $r$ is the interatomic distance, $\varepsilon$ is the potential well depth and $\sigma$ is the interatomic distance at which the potential energy is zero. The Lennard-Jones potential best models Van der Waals interactions of noble gases. The first term, $\left( \frac{\sigma}{r} \right)^{12}$ represents the Pauli repulsion energy due to overlapping orbitals at close ranges. The second term, $\left( \frac{\sigma}{r} \right)^{6}$, is the attractive long range dispersion force. The Lennard-Jones potential is shown graphically in Figure 2-6.

![Figure 2-6. The Lennard Jones Potential.](image)

**2.3.2.2 Buckingham Potential**

The Buckingham potential is a fairly simple formalism used for ionic systems. It describes the short range interaction of two non-bonded atoms with the Pauli Repulsion energy and the van der Waals interactions, as shown in Eq. (2-23), where $A$, $\rho$, and $C$ are adjustable materials parameters specific to a given bond type, i.e. M-O vs. O-O, where M is a cation and the O is the anion. The interatomic distance is given as $r$ and the long range interactions are typically handled by the Coulombic energy shown in Eq. (2-24) where $q$ is the atomic charge and $\varepsilon_0$ is the permittivity of free space.[36]
\[ U_{\text{Short}} = Ae^{-Br} - \frac{C}{r^6} \]  
\[ U_{\text{Long}} = \frac{q_i q_j}{4\pi\varepsilon_0 r} \]

**2.3.2.3 ReaxFF**

ReaxFF is a reactive force field that can describe chemical reactivity i.e. bond breaking, which non-reactive force fields are unable to do. It uses a general bond-order-dependent potential for short range interactions and van der Waals and Coulombic formulations for the long range interactions. The bond-order-dependent formalism includes central force components and contributions from local perturbations (bond, angle, torsion, etc.). The general form of the total energy \( U_{\text{Tot}} \) is given in as

\[ U_{\text{Tot}} = E_{\text{bond}} + E_{\overline{\text{over}}} + E_{\text{under}} + E_{\text{val}} + E_{\text{pen}} + E_{\text{tors}} + E_{\text{conj}} + E_{\text{vdWaals}} + E_{\text{Coulomb}} \]  

where \( E_{\text{bond}} \) is the bond-order central force contribution, \( E_{\overline{\text{over}}} \) and \( E_{\text{under}} \) are the energies contributed from over-coordination and under-coordination respectively. \( E_{\text{val}} \) represents the valance angle energy contribution while \( E_{\text{pen}} \) is the energy penalty associated with two double bonds sharing an atom in a valency angle. \( E_{\text{tors}} \) accounts for the energy correction as the bond order approaches zero or one based on the torsion angle, and \( E_{\text{conj}} \) accounts for the energy of conjugated systems such as in aromatic systems. \( E_{\text{vdWaals}} \) represents the non-bonded van der Waals energy contribution and \( E_{\text{Coulomb}} \) represents the energy contributed by charging effects.

\[ E_{\text{bond}} = -D_e \cdot BO_{ij} \cdot \exp \left[ p_{be,1} \left( 1 - BO_{ij}^{p_{be,1}} \right) \right] \]  
\[ BO_{ij} = \exp \left[ p_{bo,1} \cdot \left( \frac{r_{ij}}{r_o} \right)^{p_{bo,2}} \right] + \exp \left[ p_{bo,3} \cdot \left( \frac{r_{ij}}{r_o} \right)^{p_{bo,4}} \right] \]  
\[ + \exp \left[ p_{bo,5} \cdot \left( \frac{r_{ij}}{r_o} \right)^{p_{bo,6}} \right] \]
The short-range force field $E_{\text{bond}}$ is shown in greater detail in Eq. (2-26), where $D_0$ and $p_{be,1}$ are a fitted parameters. BO$_{ij}$ is the bond order and is given in Eq.(2-27), where $p_{bo}$ is a fitted parameter, $r_{ij}$ is the equilibrium bond length for the different types of bonds, and $r_o$ is the current bond length. ReaxFF is used in this work as validation of the COMB3 fitting work.

### 2.3.2.4 Charge Optimized Many Body Potential (COMB)

As with ReaxFF, the COMB3 formalism is complex because it attempts to capture a range of interaction types (metallic, covalent and ionic) within a single approach; the COMB3 potential will be used extensively in this work. We provide a brief outline here; a complete description can be found elsewhere [13]. As shown in Eq. (2-28), the total potential energy of a system ($U_{\text{Tot}}$) is given as the sum of the electrostatic energy ($U_{\text{Ele}}$), the short-range energy ($U_{\text{Short}}$), the Van der Waals energy ($U_{\text{vdW}}$) and a correction term ($U_{\text{Corr}}$):

$$U_{\text{Tot}} = U_{\text{Ele}}(q, r) + U_{\text{Short}}(q, r) + U_{\text{vdW}}(r) + U_{\text{Corr}}(i, j, k)$$ (2-28)

A more detailed form of the electrostatic energy is given in Eq.(2-29). $U_{q}$ is the sum of the energy to form a charge which takes into account the electron affinity, ionization energy and the change in electronegativity and chemical hardness as a function of environment [43], the charge-charge interactions ($U_{qq}$) which is the integration over Streitz and Mintmire style charge densities of two atoms[44] and the charge-nuclear interactions ($U_{qZ}$).

$$U_{\text{Ele}}(q, r) = U_{q}(q, r) + U_{qq}(q, r) + U_{qZ}(q, r) + U_{\text{Polar}}(q, r)$$ (2-29)

The latter two terms are implemented via the Wolf direct summation method[45]. The energy associated with the polarizability is given by $U_{\text{Polar}}$ which represents the
relative tendency of a charge distribution to be distorted in the presence of an external electric field and employs the fluctuation dipole model of Stern et al.[46]

The short-range interactions take the form of an extended Tersoff-like potential as shown in Eq.(2-30), in which the short range interactions are modified by a charge dependent correction term.

\[
U_{\text{Short}}(q, r) = \sum_i \sum_{j>i} \left( F_c(r_{ij}) \left( V_R(r_{ij}, q_i, q_j) \right) \right.
\]

\[
- B_{ij} V_A(r_{ij}, q_i, q_j) \right)
\]

(2-30)

Here, \( F_c \) is the cutoff function \( V_R \) is the repulsive term, \( V_A \) is the attractive term, and \( B_{ij} \) is the bond order function. The bond order function is shown in Eq.(2-31) where \( \xi \) is an asymmetric fitted parameter that weakens the longer bond length if \( r_{ij} \) is not equal to \( r_{ik} \); \( g_{ij} \) is the angular formalism, taken here to be a sixth-order polynomial, and \( P_{ij} \) is the coordination function.

\[
B_{ij} = \left\{ 1 + \left[ \sum_{k \neq ij}^N \left[ F_c(r_{ik}) \cdot \xi(r_{ij}, r_{ik}) \cdot g_{ij}(\cos(\Theta_{ijk})) + P_{ij} \right] \right]^{\eta_i} \right\}^{-1/2\eta_i}
\]

(2-31)

From the first three terms in Eq. (2-28), there are approximately 50 adjustable parameters available for fitting for one set of dissimilar atomic species. The long-range interactions are captured by a classic Lennard-Jones Potential, as shown previously in Eq. (2-22). The correction term, as defined by Liang et al.[13], is shown in Eq. (2-32) and consists of a sixth order Legendre polynomial \( (K_{L,Pn}) \) that provides an energy penalty as a function of bond angle.
\[ U_{\text{Corr}}(\cos(\theta_{ijk})) = \sum_{n=1}^{6} K_{LPn} \cos(\theta_{ijk}) \] 

\[ + V_{BB}(i, j, k) \] 

(2-32)

Legendre polynomials are symmetric around the origin (90\(^\circ\)) which is not altogether physical, so a bond bending term \((V_{BB})\) is added to add an asymmetric penalty to the energy function. This form was recently updated to a simpler sixth order polynomial which is available in LAMMPS:

\[ U_{\text{Corr}}(\cos(\theta_{ijk})) = \sum_{n=1}^{6} b_{ijk}^{anga,n} \cos(\theta_{ijk})^n \] 

(2-33)

The two forms of the three body correction term are interchangeable; both are available within the POSMat framework, which will be discussed in more detail in Chapter 4. The three body correction term is an angular function, which is dependent on three elemental species, and allows for the distinction between similar phases such as hexagonal closed packed and face centered cubic phases, as well as increased accuracy in ternary potentials that are necessary to model hydrocarbon systems.
CHAPTER 3
FITTING METHODOLOGIES

3.1 Background

The development of an interatomic potential is a complex undertaking.[47] While literature describing the capabilities and limits of various potentials is widely available[7, 8, 10, 13, 35, 36, 40, 48-52], the strategies and procedures used in the creation of such potentials are not as widely available. The force-matching method first proposed by Ercolessi and Adams is one fitting method in which the interatomic forces within a structure are calculated from DFT and targeted[53]. Another fitting method developed for binary embedded atom potentials involves the use of established elemental potentials and the fitting of a limited number of parameters for the cross potential to a small database of DFT calculations.[54] Finally another fitting method for the modified embedded atom method potential developed a parameter set using five cubic splines with five parameters each.[55] In this chapter, we describe one systematic strategy for developing potentials, including general fitting procedures, the development of training sets, discussions of weighting schemes for cost functions, a brief overview of optimization strategies and approaches to finalizing the potential. The discussion is presented in the context of the COMB3 potential because it is one of the more complex formalisms and thus illustrates key issues and strategies associated with the approach.

3.2 Overview of Potential Development

This section outlines the general potential fitting strategy, illustrated in Figure 3-1. The target energies, properties and structures briefly mentioned in this section will be

---

discussed in greater detail in subsequent sections. These targets should generally come from experimental values when available. When experimental values are not available, electronic-structure calculations are typically substituted. In particular, higher level QC or hybrid methods are generally preferred for molecular systems, while DFT methods are generally used for condensed phases.

Figure 3-1. A general fitting procedure, showing the order in which the parameter should be fit and the structures used to fit them.

For molecular systems, QC calculations or hybrid methods can usually provide a higher level of materials fidelity than DFT calculations. However, DFT calculations are generally more reliable for condensed phases. Since, the COMB3 potential is primarily focused on condensed phases, we chose to use DFT calculations only, so as to provide
a consistent fitting database; other potential schemes that are more focused on molecular systems might chose to develop databases from QC calculations.

A potential is given as a set of mathematical functions for the energy of the system that describes the interatomic interactions. Each of the terms in the potential typically has associated parameters that provide the materials specificity. Developing potentials for a specific system of interest requires determining a set of parameters, which describes the system with the desired accuracy.

A powerful strategy for fitting a potential involves the elimination of variables in the energy formalism and focusing on a small number of parameters at a time. This is achieved by analyzing the simplest systems first and then slowly adding increasingly complex systems with more complex physics, which bring into play additional terms and their associated parameters.

In some cases, the system for which the potential is to be developed may contain elements that have already been parameterized in the context of other materials. To ensure the integrity and transferability of the potentials, the relevant elemental parameters are taken from the previous potential. This insures consistency in the energy calculations for heterogeneous systems that may include more than one binary system.

Elemental systems are in neutral charge states; therefore, they are ideal starting points since charge–related terms in the potential do not contribute to the total energy. Under these conditions, even a potential as complex as the COMB formalism, reduces to a much simpler form with a significantly smaller number of parameters. In this case
the interaction energy can be written schematically in the form of a Tersoff-like potential[38]:

\[ U_{\text{short}}(r) = \sum_i \sum_{j>i} \left( F_c(r_{ij}) \left( V_R(r_{ij}) - B_{ij} V_A(r_{ij}) \right) \right) \]  \tag{3-1}

where \( V_R \) is the repulsive term and \( V_A \) is the attractive term. The bond order term, \( B_{ij} \), can be quite complex and contains the many-body physics of the system. It should be noted that while at this stage of the fitting only parameters of the Tersoff-like potential are being fit, COMB3 in fact utilizes an extended Tersoff scheme that resembles the REBO+MoS\(_2\) potential[7] which has far more flexibility than the original Tersoff with additional parameters that may be utilized near the end of a fit to achieve higher accuracy when warranted. Even with an elemental system and a reduced parameter space to explore, it is still important to have reasonable first guesses for the parameters that allow further parameter optimization to take place. It can, therefore, be helpful to use an existing potential set for an element that is similar in properties to the element being fit as a generic starting point in parameter space.

Dimers are the ideal initial structure for parameter development due to their simplicity. Even for systems in which dimers are not physically realizable, it is useful to begin with dimers, with energies determined from DFT calculations. With only a single bond, the bond order for a dimer simplifies to unity (\( B_{ij}=1 \)), leaving only the parameters in the attractive and repulsive terms, \( V_R(r_{ij}) \) and \( V_A(r_{ij}) \), to be fitted. Electronic-structure calculations are used to determine the dependence of the energy of the dimer on the bond length. The use of multiple data points, i.e. various bond lengths or angles, allows not only the energy, but also its derivatives to be determined; these derivatives are associated with key properties, including the melting temperature in the case of the
second derivative and thermal expansion in the case of the third derivative. The parameters of the repulsive and attractive terms can then be fit using this energy curve. Adding trimers introduces a bond angle into the system; trimer energy vs. bond angle scans produce another set of data points to be included in the training database. These additional data points allow additional parameters in the bond order function to be fit. Using data points from dimer or trimer structures will not result in an optimal parameter set for all systems but does restrict the parameter space for a complete parameter fit without a large expenditure of effort by the potential builder or the use of a large amount of computational time.

Data from more realistic and complex structures can now be included in the training database to refine the parameter set generated in the previous step for each element. For molecular systems these may include the addition of more complex molecules, while for metals condensed phase structures are added. While, the experimentally stable phase or phases of the structure are, of course, of primary interest, it is useful to also include other condensed phases to the training database as they typically manifest coordination environments which, while different from the experimentally accessible phases, may appear in defect structures such has point defects, dislocations and grain boundaries. Moreover, it is also important to verify that the experimental phase is indeed the lowest energy structure. By including the cohesive energy and the phase order data, the attractive and repulsive parameters can then be refined. Surfaces, structures containing defects, or other structures that display coordination environments different from the equilibrium structure can also be included in the training database to refine the bond order parameters. At this point, a viable
potential for the elemental system will have been obtained. This process should be
followed for all of the element types in the materials of interest. For example, the
development of a potential for alumina would require the development of potentials for
aluminum and molecular oxygen separately.

Having obtained potentials for the relevant elemental systems, one can now
begin to fit parameters for multicomponent systems. Such multicomponent systems
introduce new interatomic interactions: for example, in alumina Al – O interactions now
need to be considered. These interactions will generally involve charge transfer from
one ion to the other; in this case leading to positively charged Al and negatively charged
O. Thus the attractive and repulsive terms considered above are inadequate to describe
the interactions, and electrostatic interactions must also be considered.

In the spirit of starting with simple systems before addressing more complex
systems, fitting the electrostatic parameters involves the consideration of increasingly
complex charge contributions to the energy. Since the COMB potential needs to
describe environments in which an element is charged and environments in which an
element is not charged, it is necessary to first consider the energetics associated with
the ionization of each element in isolation.

The limit of a single, charged atom reduces the electrostatic energy to just the
ionization energy, as seen in the self-energy, $U_{self}$:

$$U_{self}(q, r_{ij}) = \sum_i |V_i^{ioniz}(q_i) + V_i^{field}(q_j, r_{ij})|$$  \hspace{1cm} (3-2)

Taking the terms in Eq. (3-2) in turn, the ionization energy only depends on a few
single-atom parameters. In particular, accurate values for the electron affinity and the
ionization energy are experimentally available for many elements; these can be used to
determine $V_{\text{ioniz}}$. For elements, for which such data are not available experimentally, or are incomplete, values can be determined from electronic-structure calculations. $V_{\text{field}}$ quantifies the change in atomic hardness and electronegativity with the bonding environment, which simplifies to zero in the case of a single charged atom where the total energy is the electrostatic energy given in Eq. (2-29). It is important to note that in the COMB formalism valence and nuclear charges are defined separately. Thus in Eq. (3-2) interactions of valence and nuclear charges are treated separately. The polarizability of a dimer can then be used to fit the polar contribution for the electrostatics in Eq. (2-29). The polar contribution represents the change in energy due to a distortion of the electron distribution in response to an electronic field.

The dependence of the energy contributions of charging on bonding environment can be characterized by the enthalpy of charging, $\Delta H_R$:

$$M_2 + e^{-} \xrightarrow{\Delta H_R} M_2^{-}$$  \hspace{1cm} (3-3)

where $M$ represents a generic element. $\Delta H_R$ can be indirectly determined by electronic-structure calculations of the energy of the elemental charged dimers. While neutral elemental dimers were used to fit bond-related parameters, the charged dimers and their energy vs. bond length scans can be used to fit the remaining specific charge-related terms for the individual elements. In the case of COMB this includes the parameters in the field effects term ($V_{\text{field}}$) shown in Eq. (3-2).

To determine the parameters associated with Eq. (3-2), the binary dimers are then added to the training database in a similar manner as the elemental dimers. To ensure compatibility with existing COMB potentials, these binary systems should include not only the binary dimers of the elements in the materials of interest but also
any other relevant binary dimers. For these binary dimers, energy vs. bond length scans are not necessary: only the optimized binary structures are required in the training database.

In many cases this process acts as a preliminary optimization for binary condensed phase systems of primary interest; thus the parameter set is further refined in the subsequent steps. For the ionic systems of primary interest to us, it is rarely necessary to include metal-metal binary systems into the training database. However, the inclusion of metal-metal binary dimers in this step does assure that these metal-metal interactions have been to some extent optimized. Thus existing COMB potentials are not well optimized for alloy systems; of course there are already a number of highly materials specific potentials for such alloys.[35, 54, 56]

The general method for developing potentials for binary systems is similar to that for the elemental case, the key difference being the increase in the number of parameters to be fit. Many parameters are not symmetric with bond-direction: i.e., parameter(i,j) is not necessarily equal to parameter(j,i). Therefore, the number of parameters needing to be fit for this step is essentially doubled. As in the elemental case, the pair-wise and coordination parameters are first fit to the energy curves of small binary molecular systems. Specifically, bond scans allow the pair-wise parameter to be fit; and bond-angle scans then allow the bond-order terms to be fit. Because the parameters in the binary case are directional; two angle types should be fit: in the case of an oxide this would include a M-O-M angle as well as an O-M-O angle. These parameters are then refined to reproduce the cohesive energy and phase order of both
experimental and hypothetical phases. Structures containing point defects, line defects and surface structures are then used to refine the coordination related terms.

3.3 Building the Training Database

The construction of the training database is arguably the most important step in the fitting process. The database not only determines the approach to be taken to the fitting procedure but also the materials fidelity of the final potential and the range of phenomena for which it can be expected to be applicable. Poor choices in the construction of the database, in the choice of structures or in properties and their values, will be carried through the entire optimization procedure. Should the training base be flawed, any derived potential will be correspondingly flawed.

While an interatomic potential generally has the capability to describe with some level of quantitative precision many properties of a given system, it cannot describe all of the properties of a system with high fidelity. It is therefore necessary to decide early in the development of a training database which properties are the most important, and to narrow the focus to the needs of the final application of the potential. Although it is important to have the specific application in mind, there are still certain experimental quantities that should be included in any training database. These include the cohesive or binding energy of all experimentally viable structures and the energetics associated with defect formation, surface formation, bond bending, and bond stretching.

The training database consists of position files of relatively small structures and corresponding energy data. The specific structure depends upon the property being fit and the stage of the fitting. For example, to include cohesive energies of different phases of a material, one should add position files of the corresponding phases with relatively small supercells and a data table which lists cohesive energies for each
phases. At every iteration during the fitting process, energy and/or forces of each structure in the training database should be calculated with the potential and current parameter set in order to determine the parameter set of following iteration. Since optimization requires many iterations especially for such a large parameter sets, this part of the potential development is the most computing power demanding portion of the overall process. Thus choosing the smallest possible supercells of structures improves the efficiency of the process. Figure 3-2 outlines the types of structures typically required during fitting and the stage at which these structures are used. The molecular systems that should be included were discussed at length above. For condensed-phase structures any experimentally viable structure should be included as well as any other structures that might compete with the experimentally realized structures. For instance, in elemental metals all of the common elemental crystal structures such as FCC, BCC, diamond, simple cubic and HCP should be included. Taking MO\textsubscript{2} systems as a generic binary example, it is necessary to include many different phases, among which are fluorite, rutile, anatase, brookite, \(\alpha\)-PbO\textsubscript{2} and \(\alpha\)-quartz. It is important to note that multiple compositions (e.g., MO vs. MO\textsubscript{2} vs. M\textsubscript{2}O\textsubscript{3}) can even be compared as long as the targeted phase order is analyzed in terms of the enthalpy of formation, which takes into account the stoichiometry of the structure. In contrast, the energy per atom does not take into consideration the stoichiometry of the structure; thus the energy-per-atom values for differing compositions are not comparable and cannot be used to measure relative stabilities. Fitting multiple compositions, may not always be warranted but is an
option that is available for systems that have two phases of differing stoichiometries and of equal importance.

Figure 3-2. An outline of the structures required in the training database and the order in which they should be used in the fitting.

The low-index surface structures for the experimental phase of both the elemental and binary system can also be included in the training set. For elemental systems, vacancies and various physically reasonable interstitial structures should be included. For binary systems, stoichiometry-preserving defects such as Frenkel and Schottky defects should be included. Examples of targeted properties and the associated structures are given in Table 3-1 and Table 3-2 for elemental copper and hydrocarbon systems respectively.
Table 3-1. Comparison of properties for Cu from experiment, DFT, and COMB3.[10]

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>A₀ (Å)</td>
<td>3.615</td>
<td>3.640</td>
<td>3.610</td>
</tr>
<tr>
<td>E₀ (eV/atom)</td>
<td>-3.54</td>
<td>-3.50</td>
<td>-3.58</td>
</tr>
<tr>
<td>B (GPa)</td>
<td>138</td>
<td>140</td>
<td>142</td>
</tr>
<tr>
<td>C₁₁ (GPa)</td>
<td>170</td>
<td>173</td>
<td>179</td>
</tr>
<tr>
<td>C₁₂ (GPa)</td>
<td>123</td>
<td>123</td>
<td>123</td>
</tr>
<tr>
<td>C₄₄ (GPa)</td>
<td>76</td>
<td>80</td>
<td>48</td>
</tr>
</tbody>
</table>

OTHER STRUCTURES

| ∆E (HCP) (eV/atom) | 0.006          | 0.008   |
| ∆E (BCC) (eV/atom) | 0.038          | 0.015   |
| ∆E (SC) (eV/atom)  | 0.470          | 0.572   |
| ∆E (Dia) (eV/atom) | 1.039          | 0.999   |

SURFACES

| γ (111) (mJ m⁻²) | 1780            | 1294    | 1473    |
| γ (100) (mJ m⁻²) | 1780            | 1478    | 1515    |
| γ (110) (mJ m⁻²) | 1780            | 1609    | 1620    |

POINT DEFECTS

| Vacancy (eV)      | 1.27-1.28       | 1.18    |
| Interstitial (eV) | 2.8-4.2         | 2.79    |

Table 3-2. Heats of Formation ΔH (kcal/mol) for hydrocarbons from the second-generation REBO (REBO2), ReaxFF and COMB values are given in terms of differences from the experimental values.

<table>
<thead>
<tr>
<th>Species</th>
<th>Exp[48]</th>
<th>Δ(REBO2)[7]</th>
<th>Δ(ReaxFF)[8]</th>
<th>Δ(COMB)[13]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₂</td>
<td>93.2</td>
<td>-3.34</td>
<td></td>
<td>0.96</td>
</tr>
<tr>
<td>CH₃</td>
<td>35.8</td>
<td>-0.32</td>
<td>1.11</td>
<td>0.78</td>
</tr>
<tr>
<td>Methane</td>
<td>-15.99</td>
<td>-0.71</td>
<td>3.55</td>
<td>0.77</td>
</tr>
<tr>
<td>C₂H</td>
<td>135</td>
<td>-1.58</td>
<td>-19.95</td>
<td>1.05</td>
</tr>
<tr>
<td>Acetylene</td>
<td>54.33</td>
<td>-0.37</td>
<td>8.56</td>
<td>0.81</td>
</tr>
<tr>
<td>Ethylene</td>
<td>14.52</td>
<td>-0.86</td>
<td>-3.80</td>
<td>3.72</td>
</tr>
<tr>
<td>Ethane</td>
<td>-16.52</td>
<td>-0.79</td>
<td>1.69</td>
<td>-1.21</td>
</tr>
</tbody>
</table>

Some of previously mentioned properties are available from experiment, but the majority of these properties have to be calculated using DFT. However, for properties for which experimental values are available, there is almost always some discrepancy between experimental and calculated values. For quantities for which there are no
experimental values, one must use the predictions of DFT. Thus the training set as a whole will combine experimental values with the results of DFT calculations, which may not be completely internally consistent. For example, the cohesive energy for the equilibrium crystal structure may be experimentally available and this can be a part of the training set; unfortunately, the value predicted from DFT may be somewhat different. The cohesive energies of other competing structures that do not appear in the experimental phase diagram (e.g., hypothetical BCC-Cu) are not experimentally available. Thus to establish the appropriate trend in energies DFT must be used. For this case, a reasonable approach to bringing consistency is to use the experimental cohesive energy for the experimental phase combined with the differences in energies between the hypothetical structures and the experimental phase determined by DFT. Another type of inconsistency may also develop in the database due to the temperature at which experimental values are measured. The fitting process occurs at 0 K and the DFT calculations are conducted at 0 K as well. The experimental values used in the training set should also be extrapolated to 0 K. In many instances, such values are available.

Almost any static property can be included in the fitting process, with the specific choice of properties beyond the basic properties, depending on the application of the potential. For example, the mechanical response may be better simulated by adding the elastic properties of not only the low-temperature phase but of other high-temperature phases or even of phases that are not manifested in the experimental phase diagram. Also important for mechanical properties are the stacking fault energies and the $\gamma$-surface, most particularly the unstable stacking fault energy. The energies of the low-
index surfaces of the experimentally observed phase are also typically used in the fitting, but other surfaces may be included as well if warranted. The energies of grain boundaries or other types of extended defect energies can also be added. The enthalpy of formation for molecules can be included in the training database if chemistry is important to the final application.

For each structure type (bond scans, angle scans, condensed phases and defected structures including but not limited to point defects, surfaces and boundaries), five to ten structures should be included in the training set. The precision with which the target values can be matched generally decreases with increasing number of structures, while the time required to obtain a satisfactory fitting increases. However, the robustness of the potential increases as well and the likelihood of reproducing with accuracy the properties of structures not included in your training set decreases due to the variety in bonding and charging environments included in the fitting.

The development of a self-consistent training database, with all of the required properties and structures as well as specialized properties and structures, will give the potential fitting process the best chance of convergence to a viable potential.

3.4 Cost Functions and Precision Weighting

Armed with a database of experimental and DFT quantities, it is now necessary to define a procedure to optimize the parameters in the potential to best reproduce these experimental values. The difference between experimental and the values calculated from the current potential set for each property in the training database gives the total error of the potential. Assigning weights to each property in the database according to their priority or importance to the developer results in a total cost. If we consider the total cost as a function, which takes the parameter set as an input and
outputs the total cost, the process reduces to a multi-variable optimization problem where the optimization variables are the parameters of the potential.

Parameter space can have a complicated geometry, with numerous local minima, growing exponentially more complex as the number of parameters increases. At the beginning of a fitting procedure it is impossible to predict the morphology of the parameter space. Thus, finding a local minimum that yields good physical properties can be a complicated and arduous task. The cost function is the driving force behind any optimization and has the ability to drive the optimization to unstable areas of parameter space in which parameter constraints are violated or the cost is dominated by one parameter. A generic form for the cost function is:

\[ \text{Cost}(\alpha) = \sum_i w_i (P_i(\alpha) - P_i^0)^2 \]  

(3-4)

where the summation is over the properties in the training set, \( i \) (e.g., lattice constant(s), elastic constants) based on potential parameter set \( \alpha \). An even weighting scheme is one where the costs contributed by each main property at a particular stage of fitting are of similar magnitude. This is often a good scheme to start with. The actual weight that is placed on a property is then dependent on the magnitude of the property and the precision that is necessary for the property, as illustrated for representative cases in Table 3-3. Since the quantities to be fit have different units, the weight function for each quantity will also have a different unit to make the cost function dimensionless. Applying a generic desired cost to the equation, one can now solve for the weight that should be applied to the property to achieve an even weighting scheme.
Table 3-3. A representative case for an even weighting scheme based on the magnitude of the property and the precision required of the property.

<table>
<thead>
<tr>
<th>Property</th>
<th>Magnitude of Property</th>
<th>Units</th>
<th>Expected Precision of Property in COMB3</th>
<th>Precision to Significant Digit (Magnitude x Precision)</th>
<th>Generic Magnitude of Cost contributed by property (Even Weighting Scheme)</th>
<th>Weight for Property Cost (Magnitude x Precision)^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>E_cohesive</td>
<td>\sim 10^0 eV</td>
<td></td>
<td>1%</td>
<td>0.01</td>
<td>100</td>
<td>10^6</td>
</tr>
<tr>
<td>B</td>
<td>\sim 10^2 GPa</td>
<td></td>
<td>10%</td>
<td>10</td>
<td>100</td>
<td>10^0</td>
</tr>
<tr>
<td>a</td>
<td>\sim 10^0 Å</td>
<td></td>
<td>0.5%</td>
<td>0.005</td>
<td>100</td>
<td>4 \times 10^6</td>
</tr>
<tr>
<td>E_{defect}</td>
<td>\sim 10^0 eV</td>
<td></td>
<td>20%</td>
<td>0.2</td>
<td>100</td>
<td>2.5 \times 10^3</td>
</tr>
<tr>
<td>E_{surface}</td>
<td>\sim 10^0 eV/Å^2</td>
<td></td>
<td>20%</td>
<td>0.2</td>
<td>100</td>
<td>2.5 \times 10^3</td>
</tr>
</tbody>
</table>

In reality however, only a few parameters are introduced at a time, as discussed in previous sections. This means that the costs from previous properties have already been reduced, and the costs from the newly introduced properties dominate the cost function. The cost contributed from the previous properties assures that the accuracy obtained for the newly introduced property is not at the expense of previously fit properties. By the end of each step the cost contributed by each property should once again be of the same order of magnitude.

An uneven weighting scheme is where one or two properties are over-weighted to achieve a higher precision for the properties in question. This type of scheme should be used with discretion and only after an even weighting scheme has failed. An uneven weighting scheme has a greater potential to drive a parameter set to an unstable area in parameter space because only a few properties contribute significantly to the optimization. Therefore, it is prudent to limit the degree of over-weighting.

Energies should not be the only thing that is targeted. The geometries of the structures: i.e. the lattice constant, bond length, bond angle, or c/a ratio should be
weighted and targeted as well. This can be accomplished in two ways. The geometries can be targeted directly and weighted directly or the forces present in the structure can be targeted as in the force matching method\[53\]. In the case of COMB3 both methods are used. The bond length and bond angles are targeted directly for molecules and the hydrostatic pressure is calculated and targeted in the case of condensed phase structures. For fully relaxed structures the hydrostatic pressure should be zero, therefore, a cost is contributed for structures where the pressure is not zero.

Properties are not the only thing that should contribute to the cost function. Depending on the exact formalism, there may be bounds on the parameters themselves; for example, a parameter may be required to be positive, in which case a significant cost has to be associated with negative values of the quantity. Typically, the weight assigned to these parameter constraints should result in a higher cost than those coming from the properties themselves. This acts as a guardrail of sorts to ensure that the fit does not generate completely unphysical values for specific quantities. In other cases, it might be a useful strategy to temporarily allow an intrinsically positive quantity, such as certain elastic constant, to be negative as a path through parameter space to an acceptable parameter set, in which that parameter would again be positive.

As an alternative to Eq.\((3-5)\), the cost function can be defined as:

\[
Cost(\alpha) = \frac{\sum_i w_i (P_i(\alpha) - P_i^0)^2}{(P_i^R)^2}
\]

\(3-5\)

For most properties, \(P_i^R\) in the denominator is a representative value and can be the same as the Target Value if this value is non zero. For parameters for which the target value is zero (such as certain elastic constants) or very small, a suitable representative value can easily be chosen based on reasonable physical values for
related quantities. The advantage of this representation of the cost function is that all of
the weights are dimensionless and their values directly measure the degree to which
the associated quantities need to be optimized.

3.5 Optimization Strategies

For any given definition of the cost function, the development of the potential now
becomes a classical optimization problem. Optimization schemes are discussed
extensively in the literature. Only a short review of the typical options available will be
covered here including the advantages and disadvantages of each, along with a short
discussion on the use of multiple optimization schemes in tandem.

Iterative gradient-based optimization schemes, such as the Simplex algorithm,
first proposed by Dantzig in 1947, offer a fast optimization scheme that converges to a
local minimum.[27] Gradient-based optimization schemes operate on the fact that the
derivative of the function in question is zero in a local minimum; it thus accepts steps
that minimize the derivative. Gradient-based methods do however require that the
derivatives be calculated at each iterative step; thus these methods are best used for
polynomial type optimizations where the derivative is easy to calculate. There are many
optimization problems for which the derivative may not be known, may be
computationally expensive to obtain, or for which the derivative of the cost function is
not defined at a particular point; for these cases other optimization methods are
required.[50]

The Downhill Simplex method is a heuristic method that improves on the gradient
method in that it does not require the calculation of the derivatives. First proposed by
Nelder and Mead in 1965, downhill simplex works on the premise of an n+1-dimensional
polyhedra in an n-dimensional space. The center point of the polyhedra, or geometrical
centroid of the N points in parameter space, is taken as the current parameter set at any iterative step. The “worst-case” point or points at the indices of the polyhedra can then be moved and the centroid reevaluated. In this way the polyhedra can stretch, compress, or reflect around the central “fit”. This is illustrated in Figure 3-3 for two dimensional parameter space with the cost on the vertical axis.[27, 60]

![Figure 3-3](image)

Figure 3-3. Graphical Representation of downhill simplex optimization illustrating a polyhedra contracting towards the minimum in two dimensional parameter space.

Both the gradient-based and downhill simplex method can only go downhill and thus can only find a nearby minimum in parameter space; they are thus unlikely to find the global minimum in a parameter space with a high number of dimensions.
Global optimization methods sample parameter space widely and, and thus have a higher probability of finding the global minimum. However, they generally take longer than iterative gradient based methods and there is still no guarantee that they will actually find the global minimum. Moreover, it is never possible to determine if a minimum that has been found is a global minimum; it is of course possible to identify a minimum as being only a local minimum if a lower minimum is found. Global optimization methods include stochastic methods such as direct Monte-Carlo sampling[61] and simulated annealing[62] that attempt to move in random directions through parameter space and, under certain conditions, allow steps in the optimization process that increase the cost function rather than decrease it. This can allow the transition from the one minimum to another to be found. As the optimization advances, the criterion for allowing steps that increase the cost function is tightened so that near the end of the optimization a single minimum has been found. While these methods do not guarantee the identification of a global minimum, they have been found to be effective in improved optimization.[27]

Genetic algorithms are adaptive heuristic methods, first proposed by Holland in the early 1970’s. Inspired by the process of natural selection, genetic algorithms are based on the principle of population genetics.[63] A population of possible solutions is generated as the first generation. The fitness of each parameter set or solution is evaluated against the cost function and the solutions ranked accordingly. Solutions are then probabilistically “mated” according to the previous ranking. The probabilistic selection allows for some randomness in the mating process, corresponding to random mutations, as in nature. The “offspring” become the second generation. This second
generation of solutions is of the same size as the first generation, but generally has lower values of the cost function. This process continues until the convergence criterion is met by one of the population. Genetic algorithms are powerful for extremely complex systems where other optimization techniques fail. However, like all optimization techniques finding the global minimum is not guaranteed and the time needed to complete the optimization is not consistent, i.e., the time to optimization of the same optimization can vary widely, depending on the populations that are generated during the process.[64]

It is often necessary to use more than one optimization scheme, since each has its own advantages and disadvantages. For example, using simplex to locate a reasonable area of parameter space followed by Monte Carlo to find a global minimum followed by another round of simplex to drive the fitting into the minimum is one such combination of algorithms that could result in a better fitting result than the use of either method alone. In the case of COMB using the Downhill Simplex Method has been successfully used in many elemental and electrostatic cases. However, with the increased complexity of parameter space in the binary case the Downhill Simplex Method has been less successful in that the success of the fit greatly depends on the initial values of the parameters. Recently, the use of Monte Carlo optimization schemes in conjunction with the Downhill Simplex Method has shown promise in overcoming these challenges.

Searching for the best available parameter set is one side of the problem. The other side of the problem is calculation of cost function at each iteration during optimization. Especially at the final stage of the parameter development process, the
number of parameters introduced to the optimization and the number of data points and the corresponding structures increase considerably. Thus the cost function calculation becomes the bottleneck of the optimization process. A straightforward solution to overcome this is to parallelize the cost function calculation process. Since corresponding structures in the database are independent of each other – i.e. during the calculation no communication is necessary between each task- parallelization of this part improves the over-all performance remarkably. For this purpose, we have developed an in-house code called POSMat (Potential Optimization Software for Materials). The details of the POSMat with its source code will be discussed in greater detail in a subsequent chapter. POSMat utilizes shared memory parallelization scheme to improve cost function calculation performance.

### 3.6 Testing the Parameter Set

Testing is the final step of the fitting process and is necessary to confirm that a particular parameter set is stable and viable. The primary reason for this is that the training set generally only includes static properties. Moreover, training sets typically only include structures that are defined by crystallography; that is the structures may not be at zero force and zero stress for the final parameter set. Finally, as previously stated, not all properties can be included in a fitting. While testing of other properties in the fitting may lead to less than desirable values it is extremely useful to understand the limitations of a parameter set.

A key test is to perform dynamic simulations of the energetics of all of the structures and properties in the training set to and confirm that the structures remain stable; this is best done by thermal annealing. Heating also allows the determination of the thermal expansion, an important physical property and a measure of the
anharmonicity of the system. After heating, the structure should also be cooled to see if it returns to the same crystal structure. Any property for which an experimental or DFT value is available may be also compared to the results predicted by the potential.

3.7 When to Claim Victory

Because of the vastness of the parameter space and the wide range of possible properties that might be of interest, it is not clear when to conclude that the potential fitting is complete and that a suitable parameter set has been determined. Unfortunately, there are no absolute standards, only guidelines.

It is likely that a parameterization has succeeded when a number of criteria have been met. The most important criterion is that all of the targets values in the training set are fitted to the precision given in Table 3-3, and that the performance in the testing phase is acceptable. Another important criterion is that all of the targeted trends such as the phase order or relative surface energies are correct. Testing of the potential should confirm a stable potential and observations during testing should verify the absence of unphysical behavior such as an unphysical phase change in the heating and cooling test.

In conclusion, a systematic approach to potential development was presented that lays out the current difficulties in the field along with strategies for confronting these problems. A general strategy for fitting parameters systematically was defined, in which the simplest possible systems are analyzed first with a gradual increase in complexity in the structures bringing more and more parameters into the fitting process. The properties and structures that should be included in the training set were given along with methods for shifting theoretical targets back to experiment. A discussion of weighting and optimization schemes illustrated the options available during the fitting.
process to achieve an optimal parameter space. Finally, procedures for testing and finalizing a parameter set were given.
CHAPTER 4
POTENTIAL OPTIMIZATION SOFTWARE FOR MATERIALS (POSMAT)

4.1 Background

There are numerous MD codes broadly available to the community, notably LAMMPS[65] and DL_POLY[66]; each of which includes a variety of different interatomic potentials. However, there are few tools that offer the ability to develop potentials. Development of an interatomic potential is a complex process, the difficulty of which increases with the number of fitting parameters within a given formulation, as described by Brenner et al.[47] and in the previous chapter[67]. The most widely disseminated computational package with a fitting capability is the General Utility Lattice Program (GULP), which can be used to develop most of the potential models implemented within GULP, including the Tersoff and Buckingham potentials.[68] The main focus of the GULP software, however, is the use of previously developed potentials for lattice statics calculations. The DAKOTA toolkit developed by Sandia National Laboratories is another package that could be used for the development of empirical potentials. This toolkit is a “black box” interface between analysis codes and iterative systems. It could be used to develop empirical potentials by coupling an optimization scheme with a Molecular Dynamics code. However, it was designed to handle many different problems beyond optimization and is therefore not specifically designed for the development of potentials; as a result, the targeting of specific properties requires a great deal of effort from the user.[69] In this chapter, a new tool is described for fitting empirical potentials. The Potential Optimization Software for

Materials (POSMat) package has been created to enable the systematic development of empirical potentials. It offers a number of strategies for targeting material properties and a number of optimization techniques. As described below, POSMat is configured to make it as easy as possible to use for those familiar with other relevant software packages, most particularly the LAMMPS MD software. While POSMat was designed specifically for the development of third-generation COMB (COMB3) potentials, it has also been constructed for the straightforward addition of other empirical potentials and therefore includes optimization strategies/methods.

This chapter is organized as follows. In Section 2, a brief overview for the COMB and Buckingham formalisms is given in order to demonstrate the degree of complexity of the kind of potential that POSMat can handle. Section 3 contains a discussion of the technical implementation of POSMat. Examples of input and output files are shown in Section 4. An example of a Buckingham potential fit for MgO developed using POSMat is given in Section 5 followed by a brief conclusion.

4.2 Implementation and Details

The POSMat code consists of five distinct modules: the Optimization, the Mask, the Parameters, the Energy Calculation, and the Cost Function Calculation. Figure 4-1 shows a detailed schematic of the iterative calculations performed in POSMat. The Mask and Parameter modules are accessed heavily during initialization and are used to pass the parameters between the optimizer and cost function. These five modules are addressed in turn in this section.
Figure 4-1. Schematic of the flow of calculations performed in POSMat.

POSMat is written in FORTRAN 2013 and utilizes a polymorphic, object oriented programming style. POSMat has a modular structure, which allows for the relatively simple addition of other formalisms and optimizers through the use of abstract data types, derived types that are loosely defined programming structures. We use abstract data types as placeholders with sockets for a variety of attributes, functions, and variables ready to be allocated with a desired type depending on the settings of the program. We call these abstract types ‘base types’ throughout the code. There are four base types for each module, which must be allocated during initialization; these include the parameters, the energy formalism, the mask variable that controls which parameters are allowed to change during optimization, and the optimizer. Each of these has deferred functions, which define the common processes in each type, such as reading in parameters or calculating the energy. Base types are templates for the modules of the code. At the implementation level, a derived type (object in some programming languages) in POSMat extends one of these base types and inherits deferred functions
and variable declarations of the base type. Implementations of these functions and variables can be different for any derived type. POSMat is designed in such a way that connections between modules are established via deferred functions. This design allows us to switch between derived types of the same module during runtime. As an example, derived types which implement Simplex-B and Simulated Annealing extend the same base type. Thus the user can switch between these optimizers without restarting the program. Furthermore, this design enables relatively easy implementation of new modules.

More detailed descriptions of these deferred functions will be discussed in subsequent sections. A sample of pseudocode illustrating the allocation of each of the formalism variable types is illustrated in Figure 4-2. The allocation of the optimizer is discussed in greater detail in subsequent sections.

1. READ energy formalism
2. IF formalism is available
   2.1 INITIALIZE parameter type based on formalism
   2.2 INITIALIZE energy type based on formalism
   2.3 INITIALIZE mask type based on formalism
3. ELSE
   3.1 PRINT ‘Energy Formalism unavailable’

Figure 4-2. Pseudocode illustrating the allocation of the energy formalism types.

4.2.1 Potential Optimization

The primary function of POSMat is the optimization of an empirical potential for a given material system. This is achieved via the minimization of the “cost function”, (also known as the “error function”) by optimizing the parameters of the potential function \( \alpha \) as previously defined in Eq. (3-4).
The inputted weight by which each property difference is multiplied serves a dual purpose. Firstly, it makes the error contributed by each property dimensionless and secondly, it allows the user to determine the properties that are targeted the most heavily by either increasing or decreasing the contribution from the given property to the error function. There is another error function style that normalizes the error by dividing the entire function by a representative value of the given property given previously in Eq. (3-5). Both styles are available in POSMat and may be specified in the input file with a keyword. The inputted target value for any given property, such as enthalpy of formation or elastic constants, should come from experimental values whenever possible. When experimental values are not available, electronic-structure methods at the level of density functional theory or quantum mechanics may be used to determine target values. A more detailed and thorough discussion about weighting procedures, error function styles and training set construction may be found in the previous chapter.[67]

A potential parameter set evolves from the inputted values during optimization, yielding a final set that provides a local minimum of the cost function with respect to the given target properties. POSMat currently includes Adaptive Simplex[27, 60] and Simulated Annealing[62] algorithms to govern this process. As previously explained in Chapter 3, the Downhill Adaptive Simplex method is a gradient-based method that will find the nearest minimum to the starting point with a high degree of accuracy. A global optimizer such as the Simulated Annealing algorithm may be used to sample parameter space outside of the local minima to increase the likelihood of finding a lower minimum of the cost function. Of course, even simulated annealing does not guarantee that the
global minimum will be reached. POSMat allows for these two methods to be used in tandem to reach a more highly optimized parameter set in a shorter amount of time. While both of these optimizers come with default values for generic settings such as step size, convergence criteria and tolerances, all settings can be customized by the user.

Each optimizer is developed separately as a derived type which extends or inherits the same abstract type. During runtime, the optimizer object is initialized with the desired optimizer type. The rest of the code is linked to the optimizer via deferred functions of the optimizer abstract type. As mentioned above these deferred functions are implemented according to the desired algorithm. Each optimization scheme included in POSMat requires a module that first extends the allocatable optimizer variable to the new type of optimizer and then defines two functions inherent to all of the optimizers, as shown in Figure 4-3. The first function is the **Initializer** and is called from the user_interface_module and sets up any required settings such as convergence criteria and step size. Within this function, default settings are included but all settings are customizable through the function call. The second function, the **Optimizer**, actually conducts the optimization and minimizes the error function determined in the **Cost** function call, which is allocated as shown in Figure 4-2. The `coeff` variable that is passed into the function represents an array of coefficients that are multiplied by the fitting parameters which change during optimization. Instead of parameter values, the **Optimizer** optimizes this coefficient set because every parameter in the set has a different magnitude. However, fitting coefficients instead of values enables us to define a single step size throughout the **Optimizer** function. This one-dimensional array is
therefore the same length as the number of parameters being fitted; all elements in the
array are initialized to one. Parameters are multiplied by the coefficients in this array
and evolve depending on the how this array of coefficients changes during optimization,
i.e. if a coefficient is less than one then a parameter will decrease and if a coefficient is
larger than one then the parameter will increase. This array of coefficients is changed
within the Optimizer function and passed out to the Cost function where it is applied to
the parameter set via Mask function. Of course this could be done within the Optimizer
function. However, the optimizer function was isolated from the rest of code in order to
create a black box which takes a set of coefficients and outputs those to minimize the
Cost function. This makes the future addition of other optimizer algorithms a much
simpler procedure.

1. INITIALIZE extended optimizer type
   1.1 INITIALIZE optimizer specific variables
   1.2 INITIALIZE optimizer specific initialize function
   1.3 INITIALIZE optimizer specific optimizer function
2. Optimizer Specific Initializer function
   2.1 READ settings
   2.2 READ tolerance
   2.3 SET settings variables
   2.4 SET tolerance variable
   2.5 END Initializer
3. Optimizer Specific Optimizer function
   3.1 READ Coeff
   3.2 WHILE new_tolerance < tolerance
       3.2.1 SET new coeff
       3.2.2 CALL Cost function (pass coeff)
       3.2.3 CALCULATE new_tolerance
   3.3 END Optimizer

Figure 4-3. Pseudocode illustrating the functions required for the addition of a new
optimizer using the Simplex optimizer as an example.
Both the **Initializer** and **Optimizer** functions are called from the **inputscript_reader** subroutine found in the user_interface_module. The **inputscript_reader** subroutine reads the input script line by line. Each line of the input script is read one at a time into a large character variable, \textit{cline}. We employ the open source library CHRPAK for the character parsing throughout POSMat[70-73]. Keywords in this large character variable are parsed within the function and then subsequent functions are called based on the keywords, including modular **read_optimizer** functions. Each **read_optimizer** function is responsible for parsing the rest of the keywords from the \textit{cline} variable which specifies any other settings that the user may want to specify for that particular optimization scheme. This function also includes any error messages for incorrect syntax before calling the **Initializer** and **Optimizer** functions. A generic version of a **read_optimizer** function is shown in Figure 4-4.

1. READ \textit{cline}
2. IF the word count of \textit{cline} is not correct
   2.1 PRINT ‘ERROR : Correct format of optimizer should be : ‘
   2.2 STOP
3. IF \textit{optimizer} is already allocated
   3.1 DEALLOCATE \textit{optimizer}
4. ALLOCATE \textit{optimizer}
5. ALLOCATE \textit{cost function interface}
6. READ settings from \textit{cline} variable
7. CALL \textit{optimizer Initializer} function and pass \textit{settings} variables
8. CALL \textit{Optimizer} function and pass \textit{coeff} variable

Figure 4-4. Pseudocode for a generic read_optimizer function where settings for an optimizer from the input file are read in.

For the addition of new optimization schemes, code will need to be added in two locations. First a module must be written that follows the basic pseudocode shown in
Figure 4-3. Second, a modular read_optimizer function must be added to the user_interface_module as in Figure 4-4, as well as a case statement for the optimizer keyword in the inputscript_reader subroutine.

4.2.2 Cost Function

The routine that computes the total cost is called iteratively from the Optimizer and in turn calls all of the subsequent routines needed to compute physical properties $P_j(\alpha)$ that enter into Eq. (3-4). Input files, which will be discussed in greater detail in a following section, specify the properties that contribute to the cost function, as well as appropriate weights. All of the properties currently available for targeting are summarized in Table 4-1.

Table 4-1. A summary of the properties currently available for targeting within POSMAT. Properties denoted with an * only for the Buckingham potential.

<table>
<thead>
<tr>
<th>Structure Type</th>
<th>Geometry</th>
<th>Property Type</th>
<th>Energetics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular Systems</td>
<td>Bond Length</td>
<td>Bond Length vs. Energy</td>
<td>Atomization Energy</td>
</tr>
<tr>
<td></td>
<td>Bond Angle</td>
<td>Bond Angle vs. Energy</td>
<td>Binding Energy</td>
</tr>
<tr>
<td></td>
<td>Forces</td>
<td></td>
<td>Enthalpy of Formation</td>
</tr>
<tr>
<td>Bulk Phases</td>
<td>Lattice Parameters (a,b,c)</td>
<td>Atomic Volume vs. Energy</td>
<td>Reaction Energy</td>
</tr>
<tr>
<td></td>
<td>c/a Ratio (hexagonal only)</td>
<td>Elastic Constants</td>
<td>Phase Order</td>
</tr>
<tr>
<td></td>
<td>Pressure/Stresses</td>
<td>Phonons Frequency and Trends*</td>
<td>Cohesive or Binding Energy</td>
</tr>
<tr>
<td>Defect Structure</td>
<td>Pressure/Stresses</td>
<td></td>
<td>Enthalpy of Formation</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Phase Order</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Defect Formation</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Surface Formation</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Stacking Fault Energy</td>
</tr>
</tbody>
</table>
The most basic calculation performed in this section is to call the energy and force/stress calculation for each inputted structure. The energy calculation, which will be discussed in greater detail in a subsequent section, is generally the most computationally expensive part of the code, depending on the size of the particular structure and energy formalism used. The quench option, which will also be discussed later in greater detail, is also called from this section of the code if it is specified in the input file.

Each materials structure considered is independent of every other and therefore the energy for each may be computed using a parallel computing structure. In the case of POSMat, OpenMP calls the energy calculation for each structure in parallel. It should be noted here that POSMat can calculate the elastic constants for specified structures by automatically generating structures under stresses of the appropriate symmetry.[74] If elastic constants are targeted in the fitting, these automatically generated structures are also included within the parallel energy call. The structures that are generated are strained versions of the targeted structure. In some cases the applied strain may break the symmetry of the original structure which can lead to internal relaxation and affect the calculated elastic constants, as is the case for shear stresses in silicon.[75] Therefore, the option is also available to optimize the atomic positions based on the current parameter set which minimizes forces.

After all the required properties associated with each structure are calculated, the cost associated with these properties is computed and summed and outputted directly back to the Optimizer. A detailed output for each structure, its targeted properties and the cost contributed from the property is also generated within the Cost function.
The properties available for targeting are broken down into three major categories: energetics, geometry, and bond strength (the second derivative of the energy). POSMat offers a variety of ways to target each of these general properties. This flexibility allows the user to customize the fitting process according to the needs of the materials system and the empirical potential that the user is attempting to develop. This approach also allows for the use of multiple techniques in tandem with the structural optimization (quenching) capability to facilitate the fitting process. For example, there are three methods available for targeting the geometry in bulk phases: fitting to the energy vs. lattice parameter without quenching, fitting to the pressure/stresses at a given volume without quenching, and fitting to the volume or c/a ratio (for hexagonal structures only) at zero pressure with quenching. Targeting of more complex symmetries or geometrical features has not yet been implemented, only because the problems of current interest have not required them; adding more complex symmetries is straightforward. Targeting the volume or lattice constant requires the use of the quench. Using a quench at the beginning of a fit, however, can lead to less than desirable results. In particular, forces may be so large within a structure that highly unphysical atomic rearrangements may arise. Knowing that all components of stress have to be zero at the target lattice constants and non-zero at any other lattice constants, the user can fit to these values to move to a suitable region of parameter space before directly targeting the volume or lattice constant.

The cost function is set up in a modular fashion. Each property available for targeting is classified by 'runtypes' which are read from the input file. From the 

```
cost_main
```

function, after the energy of each structure is calculated, the runtypes are
looped through and the corresponding functions are called as shown in Figure 4-5. After the calculation of the total cost, the `report_main` function is called, which outputs the results of each call to the cost function. A similar loop to the one in Figure 4-5 exists in the `report_main` function that calls subsequent functions which output properties specific to each runtype. The addition of a new targeted property would require the addition of two functions to the `cost_function_module`, one being the calculation of the property and the other being the function that outputs the results for the targeted property to the output file. It would also require a line to be added to the runtype loop shown in Figure 4-5 that calls the functions that calculates and sums the costs from the `cost_main` function and another line added to a similar loop in the `report_main` function which outputs the results of each call to the cost function.

1. DO WHILE count < n_runtype  
   1.1 SELECT runtype case  
      1.1.1 IF runtype is available  
         1.1.1.1 CALL runtype case function pass structures  
      1.1.2 ELSE  
         1.1.2.1 PRINT 'ERROR : runtype is unavailable'  
   1.2 END select

Figure 4-5. Pseudocode for calling of specialized cost functions.

4.2.3 Quenching and Energy Function

POSMat offers the ability to quench the inputted structures during optimization for increased accuracy of the fit. The quench option becomes important when there are previously fitted parameters contributing to the energy and forces of the system. For any binary system A-B that is being fit, the element specific parameters must first be developed; i.e. the A-A and B-B parameters. These element specific parameters are
held fixed during the binary fitting. However, if there are A-A or B-B interactions present in any of the structures being targeted for the binary fit, these interactions must be allowed to structurally relax so that errors are not introduced into the total energy of the system. While, as discussed above, it is not advisable to use the quench option during the initial stages of the fitting process, once a reasonable parameter set has been achieved, the addition of the quench can result in greater accuracy for targeted energies and geometries.

In the quench option, atomic position relaxation is achieved through a steepest descent method that minimizes the forces on each atom. The cell may be relaxed using the Parrinello-Rahman constant stress algorithm[76], preserving symmetry, hydrostatically, or with no constraint. During initialization the user may use default relaxation settings; however, all settings are customizable including which structures will be allowed to relaxed, the number of quench steps, the convergence criteria, how the structure is relaxed, how often the structure is relaxed, and which atoms within the structure are allowed to move.

In this first distribution of POSMat, two energy functions are provided: the COMB3 formalism and the Buckingham formalism[36] where the shifted force cutoff has been extended to include the core-shell model[77]. These two functional forms were chosen because together they necessitated the development of a computational infrastructure that can be used, or easily adapted, for a wide variety of commonly used potential forms. Other energy functional forms can easily be added. We will use POSMat in Chapter 5 to develop COMB3 potentials for the N-COH system.
The addition of other formalisms to POSMat, unlike other aspects of the code, does require the addition of a considerable amount of code depending on the complexity of the energy function. Figure 4-2 illustrated the allocation of the formalism which requires the allocation of three variable types: the energy, parameter set, and mask functions. Each of these requires a separate module for the addition of a new energy formalism.

The parameter object consists of the parameter_reader, get_functions, set_functions, ac_functions, and print_parameters functions as type bound procedures and arrays to store parameter sets values. The parameter_reader allocates the parameter arrays and reads in the parameters from the parameter file. There are four types of parameter arrays; element specific, bond specific, angle specific and tables. The data is encapsulated in the parameter object by setting these arrays as private variables within the parameter modules. This means functions outside parameter module cannot read or write to these arrays directly. Instead, other parts of the code access these arrays via get_functions and set_functions. This procedure is an example data hiding. The set_parameters function changes a parameter during the code execution to another value and is mostly used for setting the constraints on the parameters. The ac_parameters multiplies the parameters by a coefficient and is used for changing the parameter set during optimization. Lastly, the print_parameters outputs the final parameter set. Since the retrieval and setting of the parameters are keyword driven, the modification of these functions for the addition of any new formalism becomes more extensive the more parameters a formalism has. The mask variable requires two functions. One function sets flags to define which parameters will
be allowed to change during optimization while the other actually changes a parameter by calling the `ac_parameters` function discussed previously.

The energy module includes two functions. One function initializes the energy variables which includes four allocatable arrays for each structure. These arrays include the forces in the x, y and z direction and the energy for each atom within the structure. The arrays should be allocated to have length equal to the number of atoms in the structure. The second function actually loops through the atoms of the structure and calculates the energy and forces acting on each atom. At the end of the function the forces and energy are summed and stress tensor calculated.

### 4.3 Input and Output

#### 4.3.1 Parameter File

A file containing initial values of all of the energy function parameters to be fitted is required to initialize an optimization. There are three sections of the file: element specific parameters, bond specific parameters, and three-body parameters in that order. However, within each section the parameters may be specified in any order as long as all parameters are included. A line beginning with a pound sign can be used as a comment line at any point in the file so that the file may be more readable. Keywords specify which parameters are being read in and are formalism specific. An example for the elements section of a parameter file in the COMB3 format for copper is shown in Figure 4-6.

#### 4.3.2 Initialization File

The initialization file includes all of the information necessary for the optimization process. As in the parameter file, a line beginning with the pound sign is treated as a comment line. There are four major sections to the input file.
The first section reads in the structure and run type information. The run type specifies the type of properties that will be targeted. The first runtype keyword specifies the type of structure in the runtype; there are currently five main types: bulk, molecules, defect, reference, and special. The defect runtype is the umbrella runtype for any structure which is not a perfect structure and includes surfaces, dislocations, compound point defects, and stacking faults. This runtype may be used for any defected structure where the target energy is the formation energy of the defect structure as compared to a perfect defect free structure. The reference runtype includes structures that will not be targeted but are included for referencing purposes in targeting properties for other structures such as the enthalpy of formation, reaction energies, or phase order. The special runtype is for targeting extra properties for a structure that have already been included in a previous runtypes, such as elastic constants or phonon frequencies. The first runtype keyword is followed by the number of structures in the runtype. A secondary runtype may be specified to further define the properties that will be targeted. The runtype is followed by the structure file names, the target energies, the reference
structure, the weights placed on them, and the charge switch which determines if charges are equilibrated when the formalism used includes charge equilibration. The reference structure refers to targeted properties that require calculations that reference the energy of another structure, such as the phase order, surface energy or defect energy. All properties available for targeting are specified in the structure section of the input file; a representative example is given in Figure 4-7.

```
# structures 6
n_runtype 4
#
# File Path Target Ref# Weight1 Weight2 Weight3 Charge
# Energy Phase Order Geometry Switch
runtype reference 2
Database/str.Odimer -1.36 1 1.0 1.0 1.0 off
Database/str.Alfcc -3.36 2 1.0 1.0 1.0 off
runtype bulk 2 enthalpy
Database/str.alpha -17.34 3 le8 1.0 le6 on
Database/str.bixy -16.37 3 le7 le8 le5 on
runtype defect 1 2D_2
Database/str.Alsurf001 0.01 3 le7 1.0 1.0 on
runtype defect 1 1D
Database/str.VA1 0.01 3 le7 1.0 1.0 on
#
```

Figure 4-7. Sample of the structure portion of the input file for POSMat.

The second section includes keywords that augment the settings of the optimization further, as needed. This section is not mandatory but can be useful as it may include relaxation settings, charge constraints and output settings. The output settings determine how often the output file, which includes fitting details such as total cost and the target vs. computed values, is updated during optimization. The third section is the parameter section which includes the parameters that will be optimized during the fit and any constraints that will be placed on those parameters. The parameters are read in based on the same keywords used in the parameter file. The element symbol is used to specify which element or bond type is being fit and the
The keyword ‘constrain’ is used to set parameter bounds by specifying upper and lower limits on a given parameter and a weight that is applied to the cost if the parameter drifts outside of those bounds.

The fourth section is the smallest and is used to lay out the optimizer settings. A sample of both the parameter and optimizer section are shown in Figure 4-8.

```
#-----------------------------------
spline_parameters 6
spl_para/CCangle_table ang C C
spl_para/CHangle ang C H
spl_para/CCtor_table tor C C
spl_para/CCrad_table rad C C
spl_para/CCpcn_table pcn C C
spl_para/CHpcn_table pcn C H
#-----------------------------------
parameters
pair_wise C N paij pbij palfij plamij
coordination C N cosmol cosmol
coordination N C cosmol cosmol
legendre H N C p6p0 p6p1 p6p2 p6p3
#-----------------------------------
constrain paij_upper C N 1e10 6e4
constrain paij_lower C N 1e3 1
constrain pbij C N 1e20 5e3
constrain palfij C N 1e15 0.3
end_parameter
#-----------------------------------
optimizer
SA 800 0.2 10 2.0 5 50 1 500
simplexb 0.15 .01 1
end_opt
```

Figure 4-8. Parameters and Optimizer sections of the input file for POSMat.

### 4.3.3 Structure File

Every structure specified in the input file requires a structure file. Defect structures should be larger than the Columbic, or long-range cut-off. Alternatively, a small simulation cell, which can be as small as a primitive unit cell, may be used with images generated on-the-fly with which these atoms interact; this approach is used, for example, in GULP.\[68\] In the case of the COMB3 formalism, the longest range
interaction is generally the cutoff for the Columbic interactions. As in other input files, the structure file allows for comment lines starting with a pound sign. An example of a structure file is given in Figure 4-9 for a simple oxygen molecule. The first line includes the name of the structure and this header is used to specify each structure in the output. Lines 2-4 specify the box size in which each lattice direction is given as a 3 component vector in Angstroms. Line 5 specifies the number of atoms in the structure. Each line after line 5 corresponds to an atom within the structure. The first column is the atom number; atoms should be numbered in increasing sequential order. Columns 2 through 4 specify the coordinates of the atom in Cartesian coordinates. Column 5 specifies the initial charge and column 6 gives the atomic number. The last two columns specify flags for differing processes. Column 7 is the charge switch which allows charges for specific atoms to evolve during optimization and is 1 for on and 0 for off. Column 8 is the relaxation switch and allows the user to allow specific atoms to relax during optimization according to the settings specified in the input file and as in the case for the charges is 1 for on and 0 for off. In the case of the charges and relaxations, for an atom to move or change its charge, the flags must be set to ‘1’ and the settings must be specified in the input file; if either is specified incorrectly the atom will not move. Column 9, the last column, is reserved for future use and may be customized by the user as desired. Currently it is an integer variable but may be easily changed to a real number or other data type. POSMat includes a series of flags that can handle the generation of structure files and can easily convert structure files in VASP, LAMMPS, or cfg formats to the POSMat format and vice versa.
4.3.4 POSMAT.out

The output file is updated with the optimization details every iteration by default. However, the user may reduce the frequency of output to constrain the size of the output file; this is particularly useful if there are a large number of iterations. If the optimization details are not outputted at every step, the file is still updated with errors and parameter warnings as they are generated. The beginning of the detailed report gives a summary of the total cost calculated and the breakdown of where the cost is coming from, as shown in Figure 4-10. As previously mentioned, the cost is dimensionless and the percentage shown in Figure 4-10 is one way to ascertain that an optimization is progressing in a reasonable manner, i.e., the cost from one property does not dominate the fitting by being orders of magnitude larger than the other properties. The percentages in the far right column illustrate how much each property contributes to the cost at that point in the optimization; the user can then adjust the weights in the input file accordingly. Figure 4-10 shows all of the possible contributions to the cost function but if a specific property is not targeted then it will not normally show up in the detailed output.

\begin{verbatim}
header O2
hmatrix
 30.0000 0.00000 0.00000
 0.00000 30.0000 0.00000
 0.00000 0.00000 30.0000
natoms 2
 1 10.00 10.00 10.00 16 1 0 1
 2 10.00 10.00 11.21 16 1 0 1
\end{verbatim}

Figure 4-9. Sample structure file for an oxygen molecule in a large simulation box.
For every runtype section within the input file there is a detailed output section, each of which follows the same basic organization; this is illustrated in Figure 4-11. The first column includes the header name of each structure. The second, third and fourth columns are the calculated energy, the target energy and the cost contributed from the property respectively. The fifth, sixth and seventh columns include the target energy difference between the structure in question and the structure it references, the calculated difference, and the cost contributed from the energy difference. Another detailed output is also included for geometrical descriptors such as the target bond length and bond angle between the first three atoms in the structure in the case of molecular structures or the lattice parameters in the case of bulk structures and the hydrostatic pressure of the structure. This detailed output is organized in much the same way as Figure 4-11. Any targeted value within the input file will be shown in the output file as shown in Figure 4-11, in which the calculated value, the target value and
the cost calculated from the property are given. The size and scope of the output file is
dependent on the number of targeted values given in the input file.

Figure 4-11. Structure details from a sample output file.

### 4.4 MgO Buckingham Example

As a simple illustration of the fitting capabilities of POSMat we present the case
of a Buckingham Potential for MgO. There are many Buckingham potential parameter
sets available for MgO[78, 79], one of which was selected for the starting parameter
set[80]. Three structures were fitted to, along with the elastic constants for the
groundstate phase. The structures that were used were built and optimized using
Density Functional Theory approaches available in VASP[81-85]. The target energies
were calculated from the experimental enthalpy of formation of the rocksalt phase as
well as the output energies from VASP in the manner described for training set
construction in Chapter 3.3. The initial values for the targeted values are shown in

Table 4-2 as well as the calculated values for the starting Buckingham potential.
The lattice parameter was held fixed for both fittings and then relaxed completely in
LAMMPS following the fitting. For this particular fitting the rocksalt structure was
considered the most important structure and its properties were targeted the heaviest with a particular emphasis on the mechanical properties. As can be seen in Table 4-2, the new fitting shows a significant improvement in the mechanical properties especially the shear modulus.

Table 4-2. Property Values of a starting Buckingham Potential and POSMat Buckingham Potential A for MgO.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Target</th>
<th>Original Buckingham[80]</th>
<th>POSMat Buckingham</th>
</tr>
</thead>
<tbody>
<tr>
<td>ELASTIC MODULI</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ROCKSALT (GPa)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₁₁</td>
<td>306.7[86]</td>
<td>328.4</td>
<td>306.7</td>
</tr>
<tr>
<td>C₄₄</td>
<td>157.6</td>
<td>41.4</td>
<td>119.1</td>
</tr>
<tr>
<td>C₁₂</td>
<td>93.7</td>
<td>49.3</td>
<td>122.3</td>
</tr>
<tr>
<td>Bulk Modulus</td>
<td>226</td>
<td>142.3</td>
<td>183.8</td>
</tr>
<tr>
<td>Shear Modulus</td>
<td>92</td>
<td>-27.4</td>
<td>107.5</td>
</tr>
<tr>
<td>LATTICE PARAMETER (Å)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rocksalt</td>
<td>4.212</td>
<td>4.248</td>
<td>4.269</td>
</tr>
<tr>
<td>Zinc Blende</td>
<td>4.601</td>
<td>5.233</td>
<td>4.583</td>
</tr>
<tr>
<td>Cesium Chloride</td>
<td>2.109</td>
<td>2.616</td>
<td>2.309</td>
</tr>
<tr>
<td>PHASE ORDER ΔE° (ev/atom)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E_{Zinc Blende} – E_{Rocksalt} &amp; 1.475[84, 85, 87]</td>
<td>0.510</td>
<td>0.351</td>
<td></td>
</tr>
<tr>
<td>E_{Cesium Chloride} – E_{Rocksalt}</td>
<td>2.590</td>
<td>1.819</td>
<td>5.464</td>
</tr>
</tbody>
</table>

Eight fittings were run back to back utilizing the adaptive simplex algorithm discussed in previous sections. The evolution of the cost function over all of the fittings is shown in Figure 4-12. Initially, the phase order is targeted heavily and the cost is minimized quickly when only this property is targeted. Point A represents the point in the fitting when the hydrostatic pressures of each phase are also targeted. As a result, the error increases significantly at this point. The ions in the CsCl structure have very different symmetry than in the other two structures, body-centered vs. face centered,
and there is a direct competition between the minimization of pressure in this phase and
the other two phases. Point B represents the point in the fitting when elastic constants
of the rocksalt structure were added to the fitting. The remainder of the fitting (Points C-
F) included minor increases in the weights of specific properties that required greater
accuracy, which included \( C_{44} \), \( C_{12} \) and the hydrostatic pressure of the rock salt and zinc
blende structures. Accurate simultaneous fit of \( C_{44} \) and \( C_{12} \) is inherently impossible for a
pair potential such as this due to Cauchy relationship.[88] There are small spikes in the
error throughout the fitting and this is due to constraints placed on the parameters.
Every time a parameter became larger or smaller than the constraints placed on it there
is a spike in the error.

To illustrate some of the characteristics that may influence the duration and
accuracy of a fit, a second fit was conducted. A parameter set from a more recent paper
was selected[78] and the target database was simplified to only include the rock salt
structure and its elastic constants. The targeted values are shown in Table 4-3 for both
the original parameter set and the POSMat determined parameter set. With fewer
targeted properties, the final parameter set was achieved in five fittings as shown in
Figure 4-13. The elastic constants were targeted at point B as shown in Figure 4-13. As
in the previous case small spikes in error are due to constraints placed on the
parameters. Both parameter sets are given in Table 4-4 where the cutoff from the
original parameter set was used.
Figure 4-12. The minimization in error as a function of optimization step during simplex optimization A of the Buckingham Potential for MgO where point A represents the addition of targeted Pressure and B represents the addition of targeted elastic constants.

Table 4-3. Property values for a starting Buckingham Potential and POSMat Buckingham fitting B for MgO.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Target</th>
<th>Original Buckingham[78]</th>
<th>POSMat Buckingham</th>
</tr>
</thead>
<tbody>
<tr>
<td>LATTICE PARAMETER (Å)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rocksalt</td>
<td>4.212</td>
<td>4.259</td>
<td>4.249</td>
</tr>
<tr>
<td>ELASTIC MODULI ROCKSALT (GPa)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₁₁</td>
<td>306.7[86]</td>
<td>327.6</td>
<td>306.9</td>
</tr>
<tr>
<td>C₄₄</td>
<td>157.6</td>
<td>41.3</td>
<td>186.1</td>
</tr>
<tr>
<td>C₁₂</td>
<td>93.7</td>
<td>48.9</td>
<td>186.3</td>
</tr>
<tr>
<td>Bulk Modulus</td>
<td>226</td>
<td>141.8</td>
<td>226.0</td>
</tr>
<tr>
<td>Shear Modulus</td>
<td>92</td>
<td>-27.4</td>
<td>118.1</td>
</tr>
</tbody>
</table>
Figure 4-13. The minimization in error as a function of optimization step during simplex optimization B of the Buckingham Potential for MgO where point A represents the addition targeted elastic constants, point B the increase in weight on elastic constants.

Table 4-4. Fitted Parameters developed in POSMat for the Buckingham Potential for MgO.

<table>
<thead>
<tr>
<th></th>
<th>Fitting A</th>
<th>Fitting B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cutoff (Å)</td>
<td>6.000</td>
<td>5.216</td>
</tr>
<tr>
<td>Mg-O A (eV)</td>
<td>26007</td>
<td>70019</td>
</tr>
<tr>
<td>Mg-O ρ (Å)</td>
<td>0.21938</td>
<td>0.29122</td>
</tr>
<tr>
<td>Mg-O C (eV Å⁶)</td>
<td>299.981</td>
<td>288.934</td>
</tr>
<tr>
<td>O-O A (eV)</td>
<td>22370</td>
<td>33174</td>
</tr>
<tr>
<td>O-O ρ (Å)</td>
<td>0.28323</td>
<td>0.28429</td>
</tr>
<tr>
<td>O-O C (eV Å⁶)</td>
<td>17.6997</td>
<td>40.6299</td>
</tr>
<tr>
<td>q_{Mg}</td>
<td>1.7</td>
<td>1.7</td>
</tr>
<tr>
<td>q_{O}</td>
<td>-1.7</td>
<td>-1.7</td>
</tr>
</tbody>
</table>

MD simulations were conducted on the rocksalt structure using both parameter sets in order to test the stability of the parameter sets. Figure 4-14 illustrates the lattice parameter vs. temperature as compared to the starting potential and experiment. The original potential[78] was developed specifically to look at thermal expansion while
these potentials were developed with the mechanical properties in mind. Both fittings do a comparable job at reproducing the experimental thermal expansion.

![Graph showing lattice constant vs. temperature for MgO Rock Salt structure](image)

Figure 4-14. Lattice Constant vs. Temperature for the MgO Rock Salt structure for both fitting versions from POSMat, the original Buckingham potential and experiment.[78]

It should be noted here that in the case of the Buckingham potential where there are only three fitted parameters per bond type, POSMat may be more complicated than is really needed, because other methods have resulted in reasonable fits with a higher computational efficiency. However, the Buckingham potential was used for comparative purposes due to the large number of materials systems for which potentials parameter sets have been developed. POSMat has been disseminated through Computer Physics Communications program library [http://www.cpc.cs.qub.ac.uk/].
4.5 Conclusions

In this chapter we presented POSMat, a tool for the development of empirical potentials. The code has been validated by fitting a simple Buckingham potential for MgO. The capabilities available in POSMat were discussed. It is hoped that the polymorphic, object oriented code structure and user friendly input and output will simplify the difficult process of empirical potential development.
CHAPTER 5
A CHARGE OPTIMIZED MANY BODY (COMB) POTENTIAL FOR NITROGEN CONTAINING ORGANIC MOLECULES

5.1 Background

Complex polyatomic C-N-O-H molecules have a wide range of applications, including polymers[89, 90], explosives[91, 92], and organic electronics[90]. A wide variety of computational methods have been exploited to study C-N-O-H systems. As discussed in Section 2.2.3, quantum chemical methods based on the adiabatic connection method offer a high degree of materials fidelity for small molecular systems. However, in order to calculate the properties of interest for the aforementioned applications, dynamical evolution and long time and length scales are required, for which the computational load is very often too high due to the explicit description of the valence electrons of the atoms[16].

Atomic level simulations such as Molecular Dynamics (MD) using classical interatomic potentials offer an alternative to electronic level calculations by accounting for the effects of the interatomic interactions associated with the valence electrons without an explicit description of the electrons themselves. This allows for increased computational efficiency and thus for simulations with longer length and time and scales.

As discussed previously in Section 2.3, reactive potentials, unlike conventional force fields, have the capacity to describe dynamical processes such as bond breaking and formation. They also have the capacity to describe multiple bonding types and are well-suited to simulate the complex applications of complex polyatomic CNOH molecules. REBO[7, 38], MEAM[39], ReaxFF[8] and COMB3[13] (third-generation COMB) are all examples of reactive potentials which can describe complex bonding
environments. While potentials for CNOH systems have already been developed within the REBO, MEAM, and ReaxFF frameworks, each additional potential set developed in the COMB3 framework is transferable and compatible with other parameter sets, allowing the study of a wide variety of disparate systems. REBO potentials have been developed to specifically focus on carbon and carbon-oxygen systems with little investment in metal or metal oxide systems. The MEAM potential was developed to model alloys well; while parameterizations exist for NCOH systems they do not model diamond and graphite systems or unsaturated carbon molecules as these were not specifically included in the training set[93]. Also the parameter sets for the MEAM formalism are often developed by for specific targeted applications with the result that the various parameter sets are often not consistent and cannot be used with each other. The ReaxFF formalism does have charge transfer like COMB3. However, like MEAM, the parameter sets are developed for specific applications and are often not transferable.

The rest of this chapter is organized as follows: The fitting procedure used and the targeted properties for N-COH systems is given in Section 2. Section 3 summaries the predicted properties of the potential, the results of an COMB3 adsorption energy of N-COH molecular systems on Ti (0001) and TiN (001) surfaces, and the results of a dynamical deposition of atomic oxygen and molecular oxygen on a TiN(001) surface. Finally, a brief conclusion is provided in Section 4.

### 5.2 Parameterization of COMB3 for N-OCH

The COMB3 parameters for OCH systems were previously developed by Liang et al.[13] and were used for the development of the N-OCH parameter sets. The procedure used for fitting N-OCH parameters follows the basic procedure outlined in
Chapter 3, using the POSMat fitting software introduced in Chapter 4. Elemental parameters for all species were previously developed for the COMB3 formalism by Liang et al. and Cheng et al.[9, 13]. These were used as the basis of the development of the bond specific or binary parameters found here. For the development of all of the binary parameters, training sets were constructed for molecules of interest, which included experimentally stable molecules, such as NH$_3$ for N-H parameterization, and molecules that exhibit a range of bonding environments, such as CH$_2$NH and CH$_3$NH$_2$ (double versus single bond C-N bond) for the C-N parameterization. A complete list of targeted molecules is given in subsequent sections. Training sets for the parameterization included the molecular geometry, such as bond angles and lengths, and the equilibrium and non-equilibrium energetics. The binary parameter set was then optimized using the Simplex algorithm[27, 60] and simulated annealing[62] where the error in the target properties was given by the Eq. (5-1). Target energies were calculated by converting the experimental enthalpies of formation into an energy per atom (eV/atom) through the use of the general chemical reaction:

$$\frac{a}{2}N_2 + \frac{b}{2}O_2 + cC_{\text{graphite}} + \frac{d}{2}H_2 \rightarrow \Delta H_f N_aO_bC_cH_d$$

(5-1)

where the energies used on the left side of the equation are COMB3 values from our previous parameterizations for these systems, $\Delta H_f$ is an experimental value, and the energy of the molecule on the right is the target for the fitting (cohesive energy).

Throughout the remainder of the work, the cohesive energies ($N_aO_bC_cH_d$) are reported in eV/atom, as well as the enthalpies of formation ($\Delta H_f$) which are reported in kJ/mol. Both are the typical units used for reporting these properties; for reference: $1 \text{eV/atom} = 96.5 \text{kJ/mol}$. 
In order to target the bond strength and bond bending characteristics, energy versus bond length and/or bond angle curves were calculated for key molecules using B3LYP/6-311G** quantum chemical calculations introduced in Chapter 2. While such QC calculations can offer a high degree of accuracy, there generally still remains a discrepancy between the B3LYP/6-311G** values and the experimental values. In order to maintain consistency within the training database, the calculated values from the quantum chemical calculations were adjusted to better match the experimental values[67]. Specifically, the B3LYP curve was shifted up or down by the difference in energy from the electronic structure calculations and experimentally derived cohesive energy value for the equilibrium structure from Eq.(5-1) as shown in Figure 5-1.

As previously noted in Section 3.3, experimental values are more desirable than quantum chemical calculations as target values for obvious reasons. However, experimental values do not exist for all targeted properties such as bond strength (energy vs. bond length). A property such as bond strength must be calculated from
quantum chemical methods which introduces inconsistency in the fitting database when combined with experimental values. Shifting the entire energy curve is one way to account for this inconsistency. For the experimentally viable molecules used in this study, this shift was between 0.0084 eV/atom and 1.21 eV/atom, with an average of 0.138 eV/atom (13.3 kJ/mol). In the context of cohesive energies, a shift of 0.2 eV is not considered large when the expected precision in COMB3 for the property may be within 1%, as previously noted in Table 3-3. However, within the context of enthalpies of the equilibrium structure, such a shift can be very impactful. In the case of NH₃, using the B3LYP cohesive energy to calculate the enthalpy of formation in tandem with other COMB3 values as shown in Eq. (5-1) results in an enthalpy of formation of -107.4 kJ/mol as compared to the experimental value of -34.09 kJ/mol. The bond strength is targeted by specifically targeting the energy difference between non-equilibrium structures and the equilibrium structures. In the case of NH₃, the error in the bond length for the equilibrium structure is -5.4% which is within the expected accuracy for COMB3. When this error is taken into account as shown in the right side graph of Figure 5-1, it can be seen that the error in curvature near the equilibrium structure (± 0.1 Å) is less than 5% which is also within the expected accuracy of COMB3.

The energy and energy difference (bond strength) for structures close to the equilibrium bond length are weighted more heavily in the fitting. After these curves were accurately reproduced, the equilibrium structures were allowed to structurally relax during the fitting process and the bond lengths and angles were targeted directly. Charges are not directly targetable, however reasonable bounds were set on the charges for each element in the fitting and the charges were monitored.
Nitrogen-hydrogen parameters were developed first, followed by nitrogen-oxygen parameters and finally nitrogen-carbon parameters. Once the short range interactions were fit and all properties for the targeted molecules were produced within the expected precision for the COMB3 formalism, the parameterization was tested on a much larger group of molecules and the three-body term given in Eq. (2-33) was used to more accurately reproduce energies for systems containing more than two elements. The COMB3 N-COH parameters are given in Table 5-1 all of which were developed for this work. The remaining previously developed COH parameters are given for completeness in Table 5-2 and a complete list of the developed correction parameters are given in Table 5-3. The correction parameters denoted with an asterisk were developed previously, and are available in LAMMPS. All of these parameters are currently available in LAMMPS.
<table>
<thead>
<tr>
<th>Parameters</th>
<th>N-H</th>
<th>H-N</th>
<th>N-O</th>
<th>O-N</th>
<th>N-C</th>
<th>C-N</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>280.617</td>
<td>280.617</td>
<td>13110.9</td>
<td>13110.9</td>
<td>9142.53</td>
<td>9142.53</td>
</tr>
<tr>
<td>B₁</td>
<td>3.44934</td>
<td>3.44934</td>
<td>327.321</td>
<td>327.321</td>
<td>51.5103</td>
<td>51.5103</td>
</tr>
<tr>
<td>B₂</td>
<td>7.61271</td>
<td>7.61271</td>
<td>17.6785</td>
<td>17.6785</td>
<td>0.0123541</td>
<td>0.0123541</td>
</tr>
<tr>
<td>B₃</td>
<td>5.32756</td>
<td>5.32756</td>
<td>37.065</td>
<td>37.065</td>
<td>0.0053851</td>
<td>0.0053851</td>
</tr>
<tr>
<td>Λ</td>
<td>5.7607</td>
<td>5.7607</td>
<td>6.89799</td>
<td>6.89799</td>
<td>6.75861</td>
<td>6.75861</td>
</tr>
<tr>
<td>α₁</td>
<td>4.13002</td>
<td>4.13002</td>
<td>3.73064</td>
<td>3.73064</td>
<td>1.23296</td>
<td>1.23296</td>
</tr>
<tr>
<td>α₂</td>
<td>0.541527</td>
<td>0.541527</td>
<td>2.59741</td>
<td>2.59741</td>
<td>0.159932</td>
<td>0.159932</td>
</tr>
<tr>
<td>α₃</td>
<td>5.86348</td>
<td>5.86348</td>
<td>1.91364</td>
<td>1.91364</td>
<td>8.20817</td>
<td>8.20817</td>
</tr>
<tr>
<td>B</td>
<td>1.39802</td>
<td>7.41726</td>
<td>0.268183</td>
<td>0.0439581</td>
<td>0.29099</td>
<td>0</td>
</tr>
<tr>
<td>b₆</td>
<td>-0.000113</td>
<td>-0.697904</td>
<td>0.0549322</td>
<td>1.80325</td>
<td>2.1165</td>
<td>0.0209992</td>
</tr>
<tr>
<td>b₅</td>
<td>0.0008503</td>
<td>-0.251519</td>
<td>-0.0120463</td>
<td>-1.80508</td>
<td>-1.8033</td>
<td>0.141332</td>
</tr>
<tr>
<td>b₄</td>
<td>7.933</td>
<td>1.47748</td>
<td>3.38298</td>
<td>-0.32263</td>
<td>-2.5096</td>
<td>0.197857</td>
</tr>
<tr>
<td>b₃</td>
<td>2.1359</td>
<td>0.229852</td>
<td>1.85513</td>
<td>-0.0499692</td>
<td>-0.1825</td>
<td>-0.0086649</td>
</tr>
<tr>
<td>b₂</td>
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Table 5-3. COMB3 Correction parameters for Ti-N-O-C-H.

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5.2.1 Hydrides

N-H bonding exhibits a limited range of bonding environments. Nitrogen generally bonds with sp\(^3\) hybridization. The only N-H molecules with radically different bonding environments are those with less than three bonds. Due to this limited scope of environments, only three molecules were targeted during this step of the parameterization; NH, NH\(_2\), and NH\(_3\). Ammonia (NH\(_3\)) was deemed the most important molecule as it is experimentally stable and was therefore targeted more heavily than the other two molecules. The results of the targeted energy and geometries can be seen in Table 5-4 and can be compared to the B3LYP values within the same table.

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While COMB3 does not perfectly replicate the experimental values for the energetics it is not qualitatively worse than the quantum mechanical values. Bond-length versus energy curves were targeted for all three molecules as well as the bond angle versus energy curve for NH\(_2\). COMB3 reproduces the enthalpy of formation for all cases well and does a particularly good job in the case of NH\(_3\). COMB3 also reproduces
the bond length of NH$_3$ well, but slightly overestimates the bond lengths for the remaining molecules. While charges were not directly targeted during parameterization, they were monitored. It was found that the charge on nitrogen becomes less negative as the nitrogen-hydrogen bond length increases for all structures, which is consistent with electronic-structure calculations as shown in Figure 5-2 for NH.

![Figure 5-2](image)

**Figure 5-2. Charge on Nitrogen atom versus bond length for NH.**

**5.2.2 Oxides**

For the parameterization of pair-wise nitrogen-oxygen interactions, bond scans were targeted for nitric oxide (NO) and nitrogen dioxide (NO$_2$) as representative cases. While N tends towards sp3 hybridization, the stability of N-O systems are limited by the sp hybridization of oxygen. The bond-order terms for O-N-O were developed by targeting the bond angle versus energy for nitrogen dioxide. The bond-order terms for N-O-N interactions presented a more difficult challenge for targeting. While Nitrous Oxide (N$_2$O) is an experimentally viable molecule, it has a N-N-O bond angle instead of
the N-O-N bond angle desired for the development of the bond order terms, for which symmetric molecules are required. It was decided to use the previously developed nitrogen-hydrogen parameters to target the bond angle versus energy of NH$_2$-O-NH$_2$. The results for the targeted energy and properties can be seen in Table 5-5.

Table 5-5. Summary of Target Properties and COMB3 results for Nitrogen-Oxygen Parameterization

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After a parameter set was obtained, the equilibrium energy for subsequent molecules were tested to ascertain the viability of the parameter set. It was found that the target energy for nitric oxide (NO) skewed the accuracy of more experimentally viable molecules. Therefore, the energy for nitric oxide was weighted less than the energy of other molecules. However, the energy versus bond length curvature for nitric oxide was still weighed heavily. COMB3 was found to reproduce the energetics well for NO$_2$ as well as adequately describing the geometry. The bond strength was reproduced extremely well as seen in Figure 5-3. As in the previous case the charges were not directly targeted but were monitored during the fitting process. It was found that the nitrogen exhibits a positive charge which decreases as the nitrogen-oxygen bond length increases. This is consistent with electronic-structure methods for all molecules except
nitric oxide. B3LYP predicts that the nitrogen charge will increase as the nitrogen-bond length increases for nitric oxide only. This is believed to be due to the over-coordination of the oxygen in this molecule, which COMB3 was not able to replicate.

Figure 5-3. Energy versus bond length for NO and NO₂.

5.2.3 Cyanides

The carbon-nitrogen parameterization offered the greatest challenge, because single, double and triple bonds are all possible. Each of the three bond types has a distinctive bond length and bond strengths (first derivative of energy). Three molecules were chosen to target each of these bond types; HC ≡ N, H₂C=NH, and H₃C-NH₂. Only the bond scan for the double bond was targeted heavily as it was found that targeting the energy, bond length and bond strength of three different bond types did not result in a viable parameter fits. The double bond was chosen in order to maintain a balance between the energetics of the single bond and triple bond. However, this did result in a
much shorter predicted bond length in the case of the single bond. While COMB3 can accurately distinguish between the double and single bond, the shorter lengths were found to cause higher strains in molecules containing rings which will be discussed in greater detail in the subsequent section. COMB3 accurately reproduced the trend in enthalpy of formation for the three differing molecules. The enthalpy of formation for the double bond was produced the most accurately followed by the triple bond. The equilibrium energies and bond lengths for all three molecules are shown in Table 5-6.

The angular function was fit to bond angle versus energy curves for CH$_3$NHCH$_3$ and NH$_2$CH$_2$NH$_2$.

Table 5-6. Summary of Target Properties and COMB3 results for Nitrogen-Oxygen Parameterization.

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</tr>
</thead>
<tbody>
<tr>
<td>Enthalpy of Formation (kJ/mol)</td>
<td>132.38</td>
<td>162.76</td>
<td>91.2</td>
<td>82.42</td>
<td>-7.8</td>
<td>-68.89</td>
<td></td>
<td></td>
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<tr>
<td>Bond Length (Å)</td>
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<td>1.195</td>
<td>1.149</td>
<td>1.273</td>
<td>1.259</td>
<td>1.266</td>
<td>1.471</td>
<td>1.339</td>
<td>1.465</td>
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</table>

5.3 Results and Discussion

5.3.1 Fitting Results

Having parameterized the potential parameters with 12 fitting molecules, over eighty molecules were used to test the entire N-COH potential. The COMB3 vs. experimental values for enthalpy of formation values for the fitting molecules and nearly all of the test molecules are shown in Figure 5-4. A small subset of the test molecules
were found to be unstable in COMB3 and were not included in Figure 5-4 as the resulting molecule(s) and energy cannot be directly compared to experimental enthalpy of formation of the original molecule. These special cases will be addressed in greater detail later.

Figure 5-4. COMB3 (abscissa) vs experimental (ordinate) values for enthalpy of formation for N-CHO molecules. The line corresponds to a perfect match between the COMB3 and experimental results.
For all of the stable molecules the RMS Error was calculated and compared to ReaxFF as shown in Table 5-7, which shows that the RMS Errors in COMB3 are comparable to the corresponding RMS Errors for the ReaxFF potential. The most significant differences are for N-H and N-CHO, for which COMB3 shows a significant lower RMS Error; that is, the COMB3 provides a better description that the corresponding ReaxFF potential. It is remarkable that the COMB3 potential is overall is at least as good as the ReaxFF potentials because, as discussed above, the COMB3 potentials are designed to be transferable whereas the ReaxFF potentials are targeted for specific applications and display considerably less transferability.

### Table 5-7. RMS Error in the Enthalpy of Formation for various N-COH molecules.

<table>
<thead>
<tr>
<th>System</th>
<th>RMS Error (kcal/mol)</th>
<th>COMB3</th>
<th>ReaxFF[91]</th>
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</thead>
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<tr>
<td>N-H</td>
<td>8.16</td>
<td>12.83</td>
<td></td>
</tr>
<tr>
<td>N-O</td>
<td>25.92</td>
<td>20.34</td>
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<tr>
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<td>11.74</td>
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<td>15.92</td>
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</tr>
<tr>
<td>N-CH</td>
<td>40.40</td>
<td>39.24</td>
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</tr>
<tr>
<td>N-CHO</td>
<td>36.69</td>
<td>44.07</td>
<td></td>
</tr>
<tr>
<td>All N</td>
<td>34.76</td>
<td>36.90</td>
<td></td>
</tr>
</tbody>
</table>

However, the COMB3 potential did not describe all of the molecules well. These outlier molecules had one of two physical characteristics: an internal nitrogen-nitrogen bond which dissociated, or a 5-membered ring with smaller than equilibrium bond angles. The equilibrium bond angle for N-C interactions is 111° while the bond angle seen in these structures are usually around 90° to 100°. Examples of both types of structures are shown in Figure 5-5.
Figure 5-5. Properties of molecules that are not described by the COMB3 N-COH Potential well.

Bulk structures were also tested against DFT predictions. All of the structures tested were hypothetical crystalline phase for normally gaseous molecules. Although not experimentally realizable, the comparison with DFT is still instructive of the range of bonding environments that the COMB3 potential can describe. While COMB3 generally does a good job reproducing the phase order, as shown in Figure 5-6, the N-COH COMB3 potential does not quantitatively reproduce the binding energies as compared to DFT for solid phases.
5.3.2 Energy of Adsorption on Ti/TiN Surfaces

In order to accurately reproduce the molecular interactions with bulk phases the adsorption energy ($E_{\text{ads}}$) was calculated according to the Eq. (5-2) for a number of test cases where $E_1$ and $E_2$ are the energy per atom of the archetypical structures shown in Figure 5-7.

![Table](image)
\[ E_{ads} = E_2 - E_1 \] (5-2)

Figure 5-7. The structures used to calculate the energy of adsorption.

Five representative molecules were chosen that exhibited N-C, N-O, and N-H bonds. The molecules were then placed on three differing sites on the Ti(0001) surface and three sites on the TiN(001) surface in a nitrogen down and nitrogen up configuration. As previously stated in Chapter 1, the Ti related parameters used were previously developed[9, 11]. The adsorption sites are shown in greater detail in Figure 5-8. DFT calculations were conducted for approximately 30% of the geometries and the correction term given in Eq. (2-33) was used to improve the adsorption energies as compared to DFT. In comparing to the DFT adsorption values, it was deemed that the RMS or percent error was an unnecessary rubric. Small changes in adsorption energy (1-5 eV) in general doesn’t change the physics of adsorption. There are only three physical outcomes; a molecule does not adsorb (\( E_{\text{ads}} \gtrless 1\text{eV} \)), a molecule physisorbs (\(-1\text{eV} \gtrless E_{\text{ads}} \gtrless 1\text{eV} \)), or a molecule chemisorbs (\( E_{\text{ads}} \lessgtr -1\text{eV} \)).
Figure 5-8. Adsorbant sites denoted A-F(yellow) for the Ti(0001) [left] and the TiN(001) [right] where Ti atoms are grey and Nitrogen atoms are blue.

The comparison for a sub-set of the cases to DFT values is shown in Figure 5-9 where molecules that did not adsorb are highlighted light red, molecules that physisorbed are highlighted yellow, and the molecules that chemisorbed are highlighted green. For all except three cases the correct adsorption behavior was reproduced. The case that had the lowest error was the HNO molecule, N up, on the A site which only has a percent error of 3.6%. For many other cases, the error was less than 25% such as NH3/N down/on the B site, NO2/N up/on the A site, or NH3/N up/on the E site, have COMB3 adsorption energies of 1.157 eV, -5.049 eV, and 6.273 eV as compared to the DFT adsorption energies of 1.431 eV, -5.998 eV, and 5.190 eV respectively. The NH3 molecule was the simplest case to reproduce; however, the Ti-N-H correction terms had to also accommodate the energetics of HNO and HCN. For both the Ti and TiN surface the NH3 did not adsorb and the order of magnitude of the adsorption energy was correct.
Figure 5-9. Summary of the binding energies for selected geometries as compared to DFT calculations. Values are color-coded to represent the type of adsorption; red represents non-adsorbed molecules, yellow represents physisorbed molecules, and green represent chemisorbed molecule.
For the NO$_2$ molecule, the physics were once again reproduced for every case. However, due to a fundamental competition of physics between the TiN and Ti surface the magnitude was not reproduced in all cases. The nitrogen down cases on the Ti surface and the TiN surface shared similar bond angles but required dissimilar three body terms. Due to the presence of nitrogen embedded within the TiN surface, there was a far larger number of Ti-N-O angles than in the Ti surface. This resulted in disproportionate changes in the adsorption energies between the Ti and TiN surfaces as the three-body term changed. Figure 5-10 illustrates how the adsorption energy for these cases change depending on which surface was fit too. The first case illustrates the values when no three body term is used, and shows that all cases are in need of correction. The second case was fit to the adsorption energies on the Ti surface ignoring any error in the TiN surface. The third case is analogous, fitting to the TiN surface instead. The final case is a compromise between the two. Due to the eventual application for the oxidation of TiN, the adsorption energies for the TiN surface were deemed more important. While the nitrogen down cases for NO$_2$ on the Ti surface reproduce the physics, they greatly overestimate the adsorption energy.

As seen in Figure 5-9, COMB3 reproduced the physics of the HNO molecule for all cases on both surfaces. A mixture of Ti-N-O and Ti-N-H correction terms were used to achieve this balanced with the target properties of both the NH$_3$ and NO$_2$ molecules. The HCN and CN molecules proved the most difficult binding energies to reproduce. The other molecules were non-linear and offered a large variety of angles. The angular dependent correction term can use the variety of angles to differentiate the energetics of each adsorbed molecule.
Figure 5-10. The Comparison of binding energies for NO2 on both Ti and TiN surfaces based on differing correction term fits. The values are color coded to represent the types of physics present for each case; pink represent non-adsorbed molecules, yellow represent physisorbed molecules and green represent chemisorbed molecules.

The HCN and CN molecules, in many cases had the exact the same angular geometry but had different targeted physics. It was decided that the CN molecule binding energy was more important, because it represents a more realistic bonding environment. A summary of the binding energies for all of the molecules on each site in both the nitrogen up and nitrogen down configuration is shown in Figure 5-11. The graph is color coded in a similar manner to Figure 5-9 and Figure 5-10 in order to show
the physics represented by each molecule. The majority of cases exhibited either a physisorbed or chemisorbed behavior. The molecules with hydrogen exhibited a repulsive property when the hydrogen was positioned towards the surface with only a few exceptions. Those exceptions included configurations where another chemical species came within the energy cutoff for that species and Ti.

![Figure 5-11](image)

*Figure 5-11. Summary of the binding energies for all molecules tested in COMB3 for all Adsorption Sites.*

### 5.4 Adsorption of Oxygen Atoms and Molecules on TiN(001)

The adsorption of oxygen atoms on the TiN surface plays a crucial role in the TiN oxidation processes\[95-97\]. Here, two MD simulations were performed to examine the adsorption of atomic and molecular oxygen on TiN(001) surface through deposition using the COMB3 potential parameter sets previously presented. In the case of atomic

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oxygen deposition, sixty oxygen atoms were deposited with an incident energy of 5 eV normal to the surface in spatially random locations. The relaxation time between subsequent oxygen atom depositions was 0.5 ps. The dimensions of the TiN surface slab were 42Å x 42Å x 63Å, where the bottom layer was fixed in their bulk lattice sites to prevent the slab from translating as a result of the deposition process. The middle eight layers of TiN were thermostated using Langevin thermostat with a damping factor of 100 (fs) applied to dissipate the excess energy from the deposited oxygen atoms and to maintain a constant surface temperature. The active region comprised the top six layers of the slab; these evolved under unconstrained equations of motion. The surface slab was equilibrated at 300 K for 10 ps prior to the deposition.

Figure 5-12 shows a snapshot from the MD simulation after sixty oxygen atoms were deposited, where 70% of the deposited O atoms stick to the surface. In particular, the preferred adsorption site for atomic oxygen is the Ti atom (site D in Figure 5-8), which was in agreement with the results from DFT calculations[98, 99].

Figure 5-12. Snapshots from MD simulations following the deposition of 60 oxygen atoms deposited on TiN (001), where grey represents Ti atoms, blue represents nitrogen atoms, and red represents oxygen atoms.
The simulations further predicted that 10% of the incident oxygen atoms rebounded from the surface, and 20% of the incident oxygen atoms formed O₂ molecules in the vacuum above the surface. In the case of the simulation of O₂ deposition, four separate simulation trajectories were considered, including one trajectory of a single oxygen molecule and three trajectories where 30 O₂ molecules were deposited on the TiN surface. In the case of the deposition of one molecule, a single oxygen molecule was given an incident energy of 5 eV per molecule and placed 5.0 Å above a TiN(001) surface slab with the same dimensions and characteristics as described above for the atomic oxygen deposition case. The oxygen molecule initially bound to a Ti atom. Subsequently, it moved to a bridge position (site F in Figure 5-8) over two Ti atoms and then dissociated, as illustrated in Figure 5-13. These results were consistent with the findings of Piscanec et al[100], who analyzed the early oxidation stages of TiN(001) by means of first-principles molecular dynamics (FPMD). Those results indicated that the bridge Ti atoms (site F) were the preferred adsorption site for the oxygen molecule. As for three separate simulations of 30 O₂ molecules, the simulation results indicated that the dissociation of oxygen molecules occurred 10% of the time, 20% of the oxygen molecules were adsorbed on the surface, and the rest scattered off of the surface and back into the vacuum. Although these simulations did not illustrate the full oxidation behavior of TiN without considering other parameters, such as variations in incident energy and working temperature, they showed the capability of the COMB3 potential to
correctly describe the chemical interactions between oxygen and the TiN surface in MD simulations.

Figure 5-13. Snapshots from MD simulations following the deposition of O2 on TiN (001). The atoms are color coded by atomic charge with the values indicated by the color bar.

**5.5 Conclusions**

This chapter presented a potential for N-COH systems that can be used within the consistent framework of COMB3 for a large variety of applications. It has been shown that the potential can accurately reproduce the energetic and geometries of a wide variety of nitrogen containing organic molecules. This shows promise for possible applications in polymers.

The potential was developed to fill an existing gap within the COMB3 potential set, for eventual applications studying the oxidation behavior of TiN. The previous work illustrates that the TiN surface can accurately simulate known oxidation behavior by reproducing DFT calculations for the binding energy of NO2 and the dynamical deposition of O2.
CHAPTER 6
OXYGEN MIGRATION ACROSS TiN/TiO$_2$ INTERFACES

6.1 Background

As previously stated in Chapter 1, understanding the oxidation behavior of TiN is of extreme importance. TiN oxidizes to form a Rutile TiO$_2$ scale except at the TiN/oxide interface where a thin gray film develops. This film consists of oxidized and reduced states of Ti oxide, including Ti$_2$O$_3$, Ti$_3$O$_5$, and TiO.[101] The presence of so many oxidation states indicates that the oxide nucleates and grows at the TiN/oxide interface instead of at the surface. Growth of an oxide scale in this case is then dependent on the diffusion of oxygen through the oxide scale and across the interface rather than on diffusion of metal cations to the surface.[2]

The evolution of the oxide scale is highly dependent on temperature. Below 800°C, the oxide scale that forms is protective; at these temperatures growth of the oxide is initially rapid but eventually slows and then stops as diffusion distances increase. Above this temperature however, unmitigated growth of the oxide can be seen in TiN due to the formation of cracks in the oxide that allows for more rapid diffusion of oxygen through the oxide scale.[101] This is due to high compressive stresses between the oxide scale and TiN substrate. An inner protective layer then forms as oxygen continues to diffuse through the porous oxide layer which eventually delaminate, causing the cycle to repeat resulting in the structure shown in Figure 6-1. The adhesive nature of the interface is not strong enough to overcome the compressive stresses, resulting in spallation.[2] Therefore there are two main properties that control the protective nature of the oxide. The first important property is the energy of adhesion. If the scale has a low energy of adhesion than the probability of delamination increases
allowing for paths of fast track diffusion of oxygen through the scale. The second important property is the energy barrier for oxygen migration across the TiN/Oxide interface. Since the growth of the oxide occurs at the interface a high energy barrier at the interface can slow the growth of the oxide.

Electronic-structure calculations at the level of DFT can be used to investigate and develop a detailed understanding of the crystalline and interface structure in complex material systems at the atomic and electronic level. Such modeling can be of particular importance in the characterization of interfaces since they are buried within a material and therefore are difficult to probe experimentally. The initial stages of oxidation of TiN have been thoroughly investigated using DFT. These investigations focus mostly on the kinetic evolution of the initial oxidation process, such as the most likely sites for adhesion of oxygen on a TiN surface, the diffusion of oxygen across the surface, and the effect of vacancy structures on the evolution of the oxide scale.[102, 103] While these studies illuminate the initial kinetic evolution of the oxide scale, they do not quantify the adhesive nature of a fully developed oxide scale or the kinetics of continued oxide growth at a developed interface.

In this work, multiple combinations of TiN and TiO$_2$ will be constructed using the Rutile and Anatase phases of TiO$_2$ and the (001) and (111) terminations of TiN. The work of adhesion will be calculated for each interface in order to gauge the protective nature of the interfaces. NEB studies then will be conducted for the diffusion of oxygen across the interfaces and the migration energy barriers will be calculated in order to gauge the likelihood of continued oxide growth within established TiN/Oxide interfaces.
6.2 Methods

The DFT calculations were performed using the Vienna ab initio Simulation Package (VASP) [81-83, 85] with the projector augmented-wave (PAW) method with the generalized-gradient approximation (GGA). The Perdew-Burke-Ernzerhof density functional (PBE)[25] was used to describe the exchange-correlation energy. The kinetic energy cutoff used was 400 eV and a 2x2x1 k-point mesh was used for the final interfacial structures where the gamma point was specified for the direction perpendicular to the interface.

The interfaces were constructed using the Rutile and Anatase phases for TiO$_2$ and the Rocksalt phase for TiN. For the oxide, the low-energy surfaces were used; (110) Rutile and the (001) Anatase shown in detail in Figure 6-2. Experimentally, these surfaces have been shown to be the most stable surfaces and their stability can be explained through the concept of autocompensation. Autocompensation predicts that the most stable surfaces are those where the dangling bonds of the anions are compensated by the dangling bonds of the cations[104]. The oxides were paired with the (001) TiN surface, the low energy surface which can also be explained by autocompensation and the (111) terminated TiN surface which is the low stress surface.

Figure 6-1. Schematic of the cross section of the oxide scale structure on TiN.[101]
While the (111) terminated TiN surface has the lowest stress, it is also the highest energy surface due to its polar nature[105]. The TiN surfaces are shown in detail in Figure 6-3.

Figure 6-2. Relaxed TiO$_2$ surfaces used to construct the TiN/Oxide Interfaces; Ti (Light Blue), Oxygen (Red)).

Figure 6-3. Relaxed TiN surfaces used to construct the TiN/Oxide Interfaces; Ti (Light Blue), Nitrogen (Purple)).
Because growth of the oxide occurs at the interface, most of the strain occurs in the oxide. Therefore, the strain was imposed on the oxide only, with the in-plane lattice parameter of the TiN fixed to its bulk value. The strain was calculated for multiple combinations of the TiN and TiO$_2$ surfaces previously presented, as shown in Figure 6-4, where the surface slabs were one unit cell thick, perpendicular to the interface. Two interfaces were chosen which minimized the strain in each direction parallel to the interfaces, while having computationally convenient small dimensions. Figure 6-4 shows the calculations used to determine the dimensions of the interface parallel to the interface where the highlighted yellow lines represent the dimensions that were selected. Strain calculations for two other possible interfaces (Rutile(110)/TiN(111) and Anatase(001)/TiN(001) were included but full interfaces were never built due to the large strains.

An appropriate thickness of each phase was determined by calculating the surface energy of increasingly thicker slabs until the surface energy approached that of previously calculated values as shown in Figure 6-5. Two termination geometries were used for the Rutile (110) surface; the stoichiometric surface and the high temperature non-stoichiometric reconstruction in which the 2-coordinated bridging oxygens are removed. The bridging oxygen atoms in the (110) termination make the surface extremely stable and energetically unreactive. It is hypothesized that the use of the reconstruction will result in a stronger work of adhesion by having a more reactive surface to adhere to. The bridging oxygens might also create a geometrical barrier to adhesion as they stick out of the surface. Two terminations were also investigated in for the TiN (111) surface; the Ti-terminated surface and the N-terminated surface. In all,
four interfacial geometries were investigated. The relaxed surfaces used to construct the four interfaces are shown in Figure 6-6.

<table>
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<th>Interface Direction</th>
<th>Oxide X TiN Dimensions</th>
<th>Oxide Length (Å)</th>
<th>TiN Length (Å)</th>
<th>% Strain</th>
<th># atoms</th>
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</table>

Figure 6-4. Interface size determination where the yellow highlighted lines represent the dimensions used to build each interface. For the bottom two structures no dimensions are highlighted because suitable dimensions could not be found that sufficiently decrease the strain.
Figure 6-5. The surface energy vs slab thickness for the surface structures used to construct the TiN/Oxide Interfaces.

Figure 6-6. Relaxed TiO$_2$ and TiN surfaces used to construct the interfaces the TiN/Oxide Interfaces; Ti (Light Blue), Oxygen (Red), Nitrogen (Purple).
6.3 Interfacial Structures

The final relaxed interfacial structures can be seen in Figure 6-7 for all of the stable interfaces. The most stable interface constructed was the Anatase (001)/TiN (111) Ti-terminated interface which exhibited the lowest stresses, shown in Table 6-1, and highest work of adhesion, as seen in Table 6-2. At the interface, the two-coordinated oxygen atoms, which in bulk are in the same plane as the Ti, were pulled towards the Ti-terminated TiN (111) surface. This behavior was not seen in the N-terminated interface. While the 2-coordinated oxygen is weakly bonded; as will be seen in subsequent sections, the oxygens did not show an inclination to relax into the interface unless positioned directly opposite a nitrogen.

![Image of interfacial structures](image)

Figure 6-7. Fully relaxed TiO$_2$ Oxide / TiN Interfaces.

Another structure was built where all of the oxygens were placed within the interface; here the oxygens not directly opposite a nitrogen relaxed back into the oxide. This resulted in the highest stresses out of all of the stable interfaces and a very low work of adhesion. These differences demonstrate the importance of termination for the TiN substrate to promote the formation of a protective oxide scale, which will resist
further oxide growth. The best way to resist growth is to prevent the formation of cracks, spallation, or delamination which a high work of adhesion can enable.

After many attempts, it was found that the stresses were too high in the stoichiometric Rutile(110)/TiN(001) structure, resulting in a failure of the DFT calculations to converge. As previously hypothesized, the 2-coordinated bridging oxygens are the cause of the high stresses and the instability. As the geometric relaxation progressed the bridging oxygens, repulsed by the TiN surface, attempted to move into the plane of Ti causing a large buildup of stresses in the b direction which became catastrophic during the relaxation. The non-stoichiometric, 1x2 reconstructed surface had considerably lower stresses than the stoichiometric counterpart, as seen in Table 6-1, due to the missing bridging oxygens and it exhibits the second highest work of adhesion seen in Table 6-2.

As previously noted, one of the primary properties that influence the protective nature of the oxide scale, is the adhesive quality of the interface. TiN is known to develop cracks and delaminate at the interface at elevated temperatures which become avenues for fast path diffusion. The trend in the work of adhesion then becomes indicative of the interface which is the most likely to be protective at elevated temperatures. The Ti-terminated TiN(111)/Anatase (001) interface exhibits the highest work of adhesion if the interfaces studied, making it the most desirable structure, while the N-terminated TiN(111)/Anatase(001) exhibits the lowest. This can be problematic as the termination may be difficult to control as oxidation progresses, especially if diffusion of oxygen across the interface is likely leading to continued growth of the oxide.
Table 6-1. Directional Stresses in fully relaxed Interfaces.

<table>
<thead>
<tr>
<th>Interface</th>
<th>Bulk Modulus (GPa)</th>
<th>Stress(GPa)</th>
<th>Externa</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>A</td>
<td>b</td>
</tr>
<tr>
<td>Rutile(110) 1x2 Reconstruction</td>
<td>218-220[106, 107]</td>
<td>0.0738</td>
<td>-0.357</td>
</tr>
<tr>
<td>TiN(001)</td>
<td>320[108]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anatase(001)</td>
<td>59-178[109]</td>
<td>-0.0541</td>
<td>0.0479</td>
</tr>
<tr>
<td>TiN(111) Ti-Terminated Anatase(001)</td>
<td>59-178[109]</td>
<td>0.136</td>
<td>0.136</td>
</tr>
<tr>
<td>TiN(111) N-Terminated</td>
<td>320[108]</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 6-2. Energetics of fully relaxed Interfaces.

<table>
<thead>
<tr>
<th>Interface</th>
<th>TiN Surface Energy</th>
<th>TiO₂ Surface Energy</th>
<th>Interfacial Energy</th>
<th>Work of Adhesion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stoichiometric</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rutile(110)</td>
<td>0.531</td>
<td>0.127</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>TiN(001)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rutile(110) 1x2 Reconstruction</td>
<td>0.531</td>
<td>1.36</td>
<td>1.46</td>
<td>0.433</td>
</tr>
<tr>
<td>TiN(001)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiN(111) Ti-Terminated Anatase(001)</td>
<td>4.88</td>
<td>0.535</td>
<td>4.12</td>
<td>1.30</td>
</tr>
<tr>
<td>TiN(111) N-Terminated</td>
<td>4.34</td>
<td>0.609</td>
<td>4.88</td>
<td>0.0766</td>
</tr>
</tbody>
</table>

6.4 Oxygen Diffusion through the Interface

The other primary property is the energy barrier for the diffusion of oxygen within the oxide and across the interface. If there is a low energy path across the interface, even if the interface is stable, unmitigated growth of the oxide is likely, especially at high temperatures where the oxygens have more energy for diffusion. Therefore, in this section we address the issue of oxygen diffuse more rapidly.

A Nudged Elastic Band (NEB) study was conducted by taking a single oxygen in each interface structure and moving it through the first layer of the TiN. For details on
the NEB method, see Section 2.2.5. For each interface, the most likely path was chosen for investigation; the one with the largest area for the oxygen to move through into the next layer of the structure. For the TiN(001) interface, the path chosen was through the cubic hole into the tetrahedral site as shown in Figure 6-8. For TiN(111) interfaces the path chosen was through the octahedral hole into the octahedral site between Ti and N layers as shown in Figure 6-9.

Figure 6-8. Schematic of the oxygen diffusion path to be investigated for the TiN(001) Interfaces where the large blue atoms are Ti, the small purple atoms are Nitrogen and the red atom is oxygen.

Figure 6-9. Schematic of the oxygen diffusion path to be investigated for the TiN(111) Interfaces where the large blue atoms are Ti, the small purple atoms are Nitrogen and the red atom is oxygen.

To test the convergence of the calculations, the evolution of the energy with the number of geometrical relaxation steps was determined for a representative transition
image for each interface. Between electronic relaxations a geometric relaxation is conducted using a conjugate gradient algorithm in order to relax the structure into its instantaneous local energy minimum as previously discussed in Section 2.2.4. As seen in Figure 6-10, the energy rapidly converges. As a compromise between accuracy and computational efficiency, in all further calculations we use five geometrical optimization steps. The difference in energy between the fifth and tenth steps (0.25 eV for the TiN(111)/Anatase(001) interface and 0.19 eV for the TiN(001)/Rutile(110) interface) was taken as an estimate of the error our estimated energies. As we shall see these estimated errors are much less than the overall energy barrier.

![Figure 6-10. Geometric Relaxation of an NEB image.](image)

The non-stoichiometric Rutile/TiN(001) interface has only 3-coordinated oxygens at the interface. The energy barrier for the migration of a 3-coordinated oxygen through the first TiN layer is 7.47 eV with an approximate error of ± 0.19 eV. As will be seen, unlike the Anatase interfaces there is an initial energy barrier for the oxygen to move out of the Rutile surface of 4.08 eV, and a transition state with the oxygen within the
interface. In the case of both Anatase interfaces, there are both 3-coordinated and a 2-coordinated oxygens. The migration barriers for both oxygens were also determined. The maximum barrier for the Ti-terminated interface was 8.63 ± 0.25 eV as compared to the Nitrogen-terminated interface which had an energy barrier of 5.21 ± 0.25 eV. In all of the cases the error is much smaller than the overall barrier and in most cases, smaller than the energy difference from one image to the next. The energy barriers may be seen for all three interfaces in Figure 6-11.

These results are consistent with the work of adhesion results. In particular, the interface with the largest work of adhesion, the Anatase(001)/TiN(111) Ti-terminated interface, also has the largest energy barrier for the migration of oxygen across the interface. The interface with the lowest energy barrier is the N-terminated interface which also has the lowest work of adhesion. These results are summarized in Table 6-3. In this case, termination is of immense importance. An oxide in connection with the Ti-terminated surface will exhibit all of the desirable properties of a protective oxide scale. However, during dynamical formation of the oxide scale, it would be impossible to control the termination at the interface.

Table 6-3. Summary of the work of adhesion and maximum migration energy barriers for oxygen across the interface for all stable interfaces.

<table>
<thead>
<tr>
<th>Interface</th>
<th>Work of Adhesion (J/m²)</th>
<th>Migration Energy Barrier (eV/atom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rutile(110) 1x2 Reconstruction</td>
<td>0.433</td>
<td>7.47 ± 0.19</td>
</tr>
<tr>
<td>TiN(001)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anatase(001)</td>
<td>1.30</td>
<td>8.63 ± 0.25</td>
</tr>
<tr>
<td>TiN(111) Ti-Terminated Anatase(001)</td>
<td>0.0766</td>
<td>5.21 ± 0.25</td>
</tr>
<tr>
<td>TiN(111) N-Terminated Anatase(001)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 6-11. Energy barrier for oxygen migration across all three interfaces.
6.5 Conclusions

Two properties are important in the development of a protective oxide scale in TiN/Oxide systems. First, the interfaces need to exhibit a high work of energy to avoid spallation and the formation of a lamellar structure previously shown in Figure 6-1. Second, the interface itself needs to act as a barrier to further oxidation by exhibiting high migration barriers for the movement of oxygen across the interface. It was found that the interfacial system that exhibited the best qualities for the formation of a protective oxide scale was the TiN(111) Ti-terminated surface having both the highest work of adhesion and the highest energy barrier. However, termination is of extreme importance in this case. The N-terminated surface exhibited the worst qualities for the formation of a protective oxide scale. In all cases, the energy barrier is certainly high enough to prevent continued growth of the oxide within a stable interface. Therefore, the limiting property becomes the work of adhesion, of which the N-terminated surface exhibited the worst. In an interface with a low work of adhesion, delamination is likely which creates fast paths for diffusion and unmitigated growth of the oxide. If the termination can be controlled at the interface during the initial stages of oxidation then the TiN(111) Ti-terminated/Anatase(001). The TiN(001)/non-stoichiometric Rutile(110) has the second highest work of adhesion and could offer a viable alternative to the TiN(111) as the interfacial structure would be easier to control.
CHAPTER 7
SUMMARY OF WORK

7.1 General Implications

This work has addressed the need for a systematic methodology for the development of empirical potentials within a consistent framework for the investigations of heterogeneous materials. While the specific research was aimed at looking at the oxidation behavior of nitrogen containing systems, this work has implications beyond the material system presented here and extends to the entire empirical potential development community. While, there are many published potentials for a wide array of empirical potentials, the methodology and tools used to create the potentials are often not disseminated. By developing tools such as POSMat and releasing a guide for the development of empirical potentials, it is hoped that the development time required can be shortened and the effectiveness of the developed potentials can be increased.

This work also used the fitting methodologies and tools to create a COMB3 potential for N-COH systems. The N-COH potential developed within this work does a comparable job to QC calculations and ReaxFF, reproducing the physics of a wide variety of N-COH molecules containing a variety of bonding environments. These potentials were developed in order to fill existing gaps within the COMB3 potential sets for the purpose of looking at the oxidation behavior of TiN. However, the N-COH potential has broader applications than that of oxidation of TiN. It can also be used in the oxidation of TiC or TiNxC1-x systems. In addition, it can also be used to investigate polymeric applications as the potential did a reasonable job reproducing the enthalpy of formation of the larger molecules.
Finally, DFT was used to investigate the protective nature of TiN/oxide interfaces. It shows the importance of termination for oxidation properties elucidates the physics that can enhance or impair the protectiveness of the oxide scale. Such information could augment experimental attempts to improve the oxidation behavior of TiN for high temperature applications. It also lays the groundwork for future investigations into other possible TiN/Oxide interfacial structures. Such structures could include other TiN surface terminations such as the (110) surface as well as other stoichiometries for Ti such as TiO or Ti$_2$O$_3$.

7.2 Future Work

While many tools have been developed and some effective practices described for use in the development of empirical potentials, there still exists considerable ambiguity and some amount of artistry in the development process; specifically, in the weighting of targeted properties. The weights chosen during the fitting process can vastly affect the effectiveness of the fit. A clear methodological strategy should be developed to better test parameter space. Such a strategy should also be integrated into fitting tools such as POSMat. While POSMat, represents an effective tool for fitting empirical potentials there is not a large array of empirical formalisms currently available within the framework. Integrating more formalisms could vastly improve the impact of the fitting tool and aid the potential development community at large.

As previously presented, COMB3 was able to simulate many properties well, however it became obvious that COMB3 was not able to reproduce all of the desired properties. Those without potential development experience might be tempted to blame the potential developer for claiming victory too soon, potential development experience
could be tempt others to blame the functional form of the empirical potential for not adequately taking into account all of the necessary physics. There are a number of reactive force fields that attempt to take all of the correct physics into account within their functional form and there is an attraction to modify the functional form of COMB3 to resemble the successful aspects of other formalisms. However, how can one be truly certain that one functional form is better than another. What is truly necessary, is uncertainty quantification for the differing functional forms available within the current reactive force field community. Such calculations could elucidate the limitations and successes of the reactive force field formalisms, which could lead to advancement and refinement of the formalisms like COMB3.

Future work for the investigation of the oxidation properties of TiN should include the newly developed N-COH potential in conjunction with previously developed COMB3 potentials. Expansion on the DFT work can probe other possible interfaces that proved too large for the DFT framework. COMB3 within MD simulations could also probe the thermodynamic dependence on the stability of these interfaces.
LIST OF REFERENCES


BIOGRAPHICAL SKETCH

Jackelyn Martinez received her Bachelor of Science in Materials Science and Engineering from the University of Florida in 2010. She then received her master’s from the same university in 2012. In 2013 Jackelyn did a summer internship with Intel where much of the preliminary work for POSMat was conducted.