Computational Modeling of Lanthanum Hexaboride Materials: Interatomic Potentials and Molecular Dynamics

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering

by

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Lanthanum hexaboride is a ceramic with current utilization as a field electron emitter in electron microscopes. Considering that ionic diffusion occurs within this substance while in operation as an electron source, this property can potentially be exploited to produce an evacuated hexaboride lattice with interesting electrical and mechanical behavior for gas storage and separation processes. Density functional theory is employed to understand and determine the energetics of this system, and pairwise interaction potentials are subsequently developed for application in a molecular dynamics framework. Lattice inversion techniques are combined with other optimization procedures to yield potentials which are able to capture the correct equilibrium energetics and lattice dynamics of the crystal at varying temperatures. Electric fields are then applied within molecular dynamics to gain insight into the underlying mechanisms involved in electromigration of the cation through the hexaboride lattice. It is found that reasonable field strengths can induce cation migration within the ceramic at lower temperatures than those required for electron emission using this simplified approach. In addition, preliminary evidence shows that coherent effects of the cation motion may aid in overcoming diffusive energetic barriers, suggesting a coupling between electrical fields and thermal energies can lead to efficiency gains in the transport process.
Keywords: Lanthanum hexaboride, lattice inversion, pair-potential development, molecular dynamics, density functional theory, electric fields, electromigration.
Nature uses only the longest threads to weave her patterns, so that each small piece of her fabric reveals the organization of the entire tapestry.

— Richard Feynman
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List of Abbreviations

Greek Symbols

\( a \) \hspace{1em} \text{Lattice Constant}
\( \delta_{ij} \) \hspace{1em} \text{Kronecker Delta}
\( E \) \hspace{1em} \text{Total Energy}
\( eV \) \hspace{1em} \text{Electron-Volt}
\( F \) \hspace{1em} \text{Force}
\( fs \) \hspace{1em} \text{Femtosecond} \( (10^{-15} \text{ s}) \)
\( H \) \hspace{1em} \text{Classical Hamiltonian}
\( h \) \hspace{1em} \text{Planck's Constant}
\( \mathcal{H} \) \hspace{1em} \text{Hamiltonian Operator}
\( \mathcal{K} \) \hspace{1em} \text{Kinetic Energy Operator}
\( k_B \) \hspace{1em} \text{Boltzmann Constant}
\( \nu \) \hspace{1em} \text{Frequency}
\( \Omega \) \hspace{1em} \text{Primitive Cell Volume}
**p**  Atomic Momentum Coordinate

\( \phi(\mathbf{r}) \)  Interatomic Potential Energy Function

**ps**  Picosecond \( (10^{-12} \text{s}) \)

\( \Psi \)  Wavefunction

**q**  Atomic/Electronic Cartesian Coordinate

\( \mathbf{r} \)  Radial Distance

\( R_y \)  Rydberg

\( T \)  Temperature

\( t \)  Time

\( \tau \)  Timestep

\( \theta_D \)  Debye Temperature

\( \mathcal{V} \)  Potential Energy Operator

\( \mathbf{v} \)  Velocity

\( \omega \)  Crystallographic Refinement Parameter

**Acronyms**

BCC  Body-Centered Cubic

BZ  Brillouin Zone

CN  Coordination Number

CPU  Central Processing Unit
DFT  Density Functional Theory

DHCP  Double-Hexagonal Close-Packed

FCC  Face-Centered Cubic

GGA  Generalized Gradient Approximation

HREELS  High-Resolution Electron Energy Loss Spectroscopy

IBZ  Irreducible Brillouin Zone

ISS  Ion Scattering Spectroscopy

LDA  Local Density Approximation

LEED  Low Energy Electron Diffraction

MD  Molecular Dynamics

MSD  Mean-Square Displacement

NMR  Nuclear Magnetic Resonance

OPW  Orthogonalized Plane-Wave

PES  Potential Energy Surface

QHA  Quasi-Harmonic Approximation

RMS  Root-Mean Square

SC  Simple Cubic

SEM  Scanning Electron Microscope

STM  Scanning Tunneling Microscope
TEM  Transmission Electron Microscope

UPF  Unified Pseudopotential Format

UPS  Ultraviolet Photoemission Spectroscopy

XAFS X-ray Absorption Fine-Structure

XPS  X-ray Photoelectron Spectroscopy
Chapter 1

Introduction

1.1 Hexaboride Materials Relevance and Applications

Boron rich solids are a class of borides having a stoichiometry of $MB_n$, where $M$ refers to a metal and $n$ is value greater than or equal to 2. These compounds have a variety of unique 2- and 3-dimensional networks, containing covalently bonded boron atoms stabilized by electron donation from the metals [131]. The distinct structures found are attributed to the electron deficient network of boron atoms, as they have only 3 electrons to fill up the four valence orbitals per atom [79]. This allows for the 3-center, 2-electron bonding typically found in boron chemistry.

One particular class of boron rich solids is the metal hexaboride, characterized by a cubic crystalline structure with $Pm\bar{3}m$ symmetry. The six boron atoms form an octahedral unit, located at the corners of a cubic lattice with a metal occupying the central site [65]. This cesium chloride-like crystal structure is relatively rigid and constant with respect to metal substitution, owing to the stability of the covalently linked boride octahedra. For rare-earth metals, small deviations to the
lattice constant do occur with changes in the 4f electron number of the metal, an effect known as lanthanide contraction. These deviations are generally found in the interoctahedral boron bonds connecting the clusters and not within the octahedra themselves [68].

Barium, calcium, strontium, and most lanthanoids have been found to form hexaboride structures [84]. Depending on the metal used, these crystals have many interesting properties that make them relevant to research today. Divalent metal cations, for instance, typically give rise to narrow gap semiconductors, such as $YbB_6$ [45, 65]. Trivalent and tetravalent ions produce a hexaboride with metallic nature ideally having 1 or 2 electrons for transport, respectively, existing in a charge conducting state [45]. Pauli-paramagnetic, ferromagnetic, diamagnetic, conductive, superconductive, semiconductive, and more complex spin-ordered hexaborides have also been discovered and characterized [84].

Due to their unique electronic properties, metal hexaborides ($MB_6$) have found use in a variety of applications such as field-electron-emitters, electrical coatings for resistors, transmission metal catalysts, high energy optical systems, and sensors for high-resolution detectors [65, 133]. High melting points, chemical stability, magnetic properties, narrow band semiconductivity, superconductivity, hardness, thermionic emission, and electron emission efficiency are among the list of reasons these are attractive materials for such utilization. The most common use for lanthanum hexaboride has been for TEM (Transmission Electron Microscope) and SEM (Scanning Electron Microscope) electron sources. Cold field emitters (such as $LaB_6$) generate a more temporally coherent and brighter electron source. Part of this is provided by the low work function of lanthanum hexaboride, which is the minimum energy required to remove an electron from the interior of the crystal to a position outside where it experiences a negligible interaction [6].
1.2 Modeling Approach and Platforms

To probe certain properties of these materials, *ab initio* electronic structure calculations are performed using the plane-wave, self-consistent field-based suite of codes from QUANTUM ESPRESSO. The open-source software package allows for the solution of optimized geometries and energy surfaces, among other properties. The calculations from density functional theory (DFT) will be performed on the lanthanum hexaboride system. Utilizing various methods, interatomic force fields can be developed from these calculations for use in the molecular dynamics (MD) code DL_POLY. With appropriate MD boundary conditions, the effects of external electric fields can then be studied.

1.3 Potential New Applications of Hexaborides

As stated previously, hexaborides have already been implemented in specific areas of industry. The purpose of this work is to gain an understanding of the electronic and mechanical behavior of hexaboride networks, allowing one to exploit certain aspects of these materials for alternative utilizations. Using suitable potentials to describe interatomic interactions, it is believed that the application of external electric fields will provide the necessary driving force required to promote cation migration at reasonable temperatures. This will produce vacancies within the lattice once the diffusive front has passed and, owing to the abnormal strength of the boron sublattice, should be relatively stable at modest temperatures. It is hypothesized that the evacuated framework will be a very high surface area adsorbent with unusual electronic behavior and potentially exceptional thermal and chemical stability. Taking advantage of these properties, the modified lattice would be ideal for such uses as gas-phase fuel storage and high temperature absorbents.
1.4 Scope and Objectives

1.4.1 Scope of Work

In order to determine novel applications for this material, a fundamental understanding of the electronic and mechanical behavior is required. This amounts to probing the atomic interactions at various energies and geometrical layouts, accurately capturing the electronic shell distortions accompanying static and dynamic perturbations such that the bulk/overall nature of lanthanum hexaboride can be reproduced. These interactions are described by a set of 3 pairwise interaction potentials and point-charges. A combination of DFT, MD, and advanced mathematical and computational methods are employed to generate the potentials.

Diffusion of lanthanum within the ceramic is a relatively rare event at moderate temperatures. A voltage potential is therefore applied to give the additional force required to overcome activation barriers for cation migration. The potentials developed are placed within a MD framework to model the material behavior under the external field, allowing a deeper look into the mechanism of electromigration within this crystal. These results will aid in the understanding and development of suitable experimental conditions to test this system in a real-world setting.

1.4.2 Objectives

1. Model lattice energies of the lanthanum hexaboride system with DFT in various geometries.

2. Develop and apply methods to produce pairwise potentials for LaB$_6$ utilizing calculated DFT data.

3. Test and optimize the interaction potentials to accurately reproduce known
4. Simulate the crystal in diverse environmental settings \(i.e.,\) temperatures and electric fields\) to probe how dynamic properties are affected by these variables.

## 1.5 Organization of this Work

The first five chapters are introductory, giving a brief synopsis of the approaches and theories used to support this work. This chapter familiarizes the reader with the aims and goals of the project. Chapter 2 provides background information related to crystallography and current experimental characterization of lanthanum hexaboride. Chapters 3 and 4 present theoretical grounds and practical considerations for DFT and MD, respectively. In addition, DFT results for lattice optimization and migration and presented at the end of Chapter 3. Chapter 5 specifies the software used in this work.

The following four chapters comprise the methodology, computations, and results. Preliminary DFT calculations are given in Chapter 6 and correlated to published results where available. Potentials are developed in Chapter 7, utilizing lattice inversions and other techniques to create a system of interactions which is able to produce desired properties. Full-scale atomistic simulations for equilibrium and non-equilibrium situations are described in Chapter 8, giving relevant data for analysis. Finally, conclusions about the system’s response to electric fields and temperature variations are drawn in Chapter 9.
Chapter 2

Lanthanum Hexaboride Structure

2.1 Lattice Models

In solid state physics and chemistry, lattice models are typically used to describe the nature of crystalline solids. These solids can be thought of as very large, single “molecules” composed of their constituent atoms/molecules and arranged in a regular fashion, giving rise to long-range order [88, 91]. When studying a crystal, two features are important for its understanding: the basis (or unit cell) and the type of lattice. From these two properties, the various regular crystals found in nature can be modeled and studied.

2.1.1 Background

In the 1840’s, French physicist Auguste Bravais introduced the lattice types in use today. Bravais found that there were only 14 ways to arrange points in physical space such that each point has an identical environment [118]. These lattices, known as the Bravais space lattices, are the geometrical arrays onto which unit cells are placed for a 3-dimensional crystal [88, 91]. Note that length scales are not de-
scribed within the framework; only points, vectors, and translation between points are given [6]. Identical unit cells of ions, atoms, molecules, or groups of molecules are situated on the lattice to create the macroscopic crystal structure [118]. The Bravais lattice is constructed so that each unit cell experiences the same field as all of the others, as each point has identical structural and orientational relationships [6].

The unit cell, or basis, is a small volume of a solid that has all of the characteristics of the particular crystal [118]. The crystal can be produced from the basis by translational repetitions onto the Bravais lattice in all three dimensions of its periodicity [91]. As a consequence, the stoichiometry of the unit cell needs to be the same as that of the bulk material. Atoms are counted within the cell such that atoms situated on the corners, edges, and faces contribute 1/8, 1/4, and 1/2 to the number of atoms within the unit cell, respectively [88].

There is a special type of unit cell, called the primitive cell, which contains precisely one lattice point (other unit cells which have greater than one lattice point are called conventional cells) [118]. The volume of a primitive cell is $1/n$, where $n$ is the density of points in the lattice [6]. Depending on the cut-off locations, various primitive cells can be constructed. One such primitive cell, known as the Wigner-Seitz cell, is formed such that each face of the cell is equidistant to every one of its nearest neighboring points on the Bravais lattice. This type of cell is important for modeling cohesion and has a special relationship to the Brillouin zone, which will be discussed in the following chapter [118].

### 2.1.2 The Cubic Bravais Lattices

For a cubic system, three types of Bravais lattices are possible: simple cubic, body-centered cubic, and face-centered cubic [91].

The most basic and familiar of the Bravais lattices is the cubic P (for primitive),
or simple cubic –see Fig. 2.1. Metals rarely display this configuration, and the alpha phase of polonium is the only known element to arrange in this fashion under normal conditions [6]. This lattice can be described as having three primitive vectors, each with a common magnitude and are orthonormal to one another [6]. The single lattice point at (0, 0, 0) and the lattice constant (distance between points) are all that are needed to specify the simple cubic structure, producing a crystal with atoms located at each of the eight corners of the lattice (Fig. 2.1) [88]. As each of the corner atoms contribute 1/8 to the total occupancy, this type of system is occupied by one atom per cubic cell and has a void fraction of 0.476 [62].

The body-centered cubic lattice (cubic I) is also well-known –see Fig. 2.2. Chromium is an example of a metal with this type of structure [118]. It is formed by two off-set simple cubic lattices, separated such that the origin of one lattice lies in the center of another [6]. The two lattice points for this structure are (0, 0, 0) and (1/2, 1/2, 1/2) [88]. Counting the number of atoms, one can find that there are a total of 2 atoms per unit
In addition to the eight corner atoms of the simple cubic type, the body-centered lattice has one atom in the center of the cube. This cell (same number as simple cubic plus the one in the center) and these fill up 68.0% of the cube [62].

The face-centered cubic cell (cubic F), also known as cubic close-packed, consists of one atom at each of the corners and one atom in the center of each of the faces of the cell (Fig. 2.3) [88]. The total occupancy is 4 atoms per cubic F cell (the six faces and eight corners contribute three atoms and one atom, respectively) and the lattice points are located at $(0,0,0)$, $(1/2,1/2,0)$, $(1/2,0,1/2)$ and $(0,1/2,1/2)$ [88]. This type of lattice allows for a 26% void (74.0% occupancy) and many metals confine themselves to this structure, as the atoms are extremely close and thus minimize their free energy through their energetic interactions (coordination number (CN) for this structure is 12) [62].
2.2 LaB$_6$ Crystal Structure

In general, the lattice structure for metal hexaborides is simple cubic with boron octahedra at each corner of the cube bonded at the apexes. The heptatonic unit cell contains six boron atoms (with anionic nature) and one metal cation. The octahedra consist of the boron atoms, with four adjacent neighbors in every octahedron and one additional neighbor on the main axes of the cube connecting to an adjacent octahedral unit for every boron atom—see Fig. 2.4. The metal cation is placed in the center of each of the cubes in the lattice [78]. Lanthanum hexaboride has the cubic cell structure of space group $O^I_h$-$Pm\bar{3}m$, in common with all of the other rare-earth hexaborides [83]. Relative lattice vector positions of the crystal structure for a typical metal hexaboride are listed in Table 2.1 for reference.

Lattice constant values have been reported in the literature from experimental and computational efforts ranging from 4.145 Å to 4.1605 Å for $LaB_6$. A list
The general structure of metal hexaborides is simple cubic with the metal ion in the center and boron atoms in hexagonal structure in each corner. The two different B—B bonds are labeled.

![LaB₆ crystal structure](image)

**Figure 2.4:** LaB₆ crystal structure.

Table 2.1: Atomic cartesian positions of MB₆ crystal structures within the unit cell. Values are given in units of the lattice constant \( a \) and the crystallographic refinement parameter, \( \omega \), ranging experimentally from 0.1995–0.1997 for the respective boron atoms within a LaB₆ lattice.

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>B</td>
<td>( \omega )</td>
<td>0.5000</td>
<td>0.5000</td>
</tr>
<tr>
<td>B</td>
<td>( 1 - \omega )</td>
<td>0.5000</td>
<td>0.5000</td>
</tr>
<tr>
<td>B</td>
<td>0.5000</td>
<td>( \omega )</td>
<td>0.5000</td>
</tr>
<tr>
<td>B</td>
<td>0.5000</td>
<td>( 1 - \omega )</td>
<td>0.5000</td>
</tr>
<tr>
<td>B</td>
<td>0.5000</td>
<td>0.5000</td>
<td>( \omega )</td>
</tr>
<tr>
<td>B</td>
<td>0.5000</td>
<td>0.5000</td>
<td>( 1 - \omega )</td>
</tr>
</tbody>
</table>

\[ \omega = \frac{\text{B-B Intercalated Bond}}{2 \times \text{Lattice Constant}} \]
of reported experimental values for lanthanum hexaboride as well as other metal hexaborides is given in Table 2.2 below.

Table 2.2 shows some interesting trends of the boride lattice structure as both the cation size and charge are varied [30, 103]. As the ionic radius increases, the lattice constant increases accordingly. The change in the boron lattice is mainly due to expansion of the interoctahedral \(B - B_{\text{interO}_h}\) distances (standard deviation of values is over twice as much as the intraoctahedral distances), although there is some lengthening of the intraoctahedral bonds as well [30]. This amounts to the octahedron cages expanding slightly while the bonds between separate cages in the lattice change their size to accommodate the larger ion. The difference in lattice constants is not linear with ionic size, as the boron network is very stable, resisting large deviations for large ions and deterring unrealistic contractions for smaller ions [103].

As lanthanum and calcium have similar lattice constants and ionic radii but differ in charge, we can compare these two to isolate the effect of charge on the boron lattice. Changing from the +2 cation (calcium) to the +3 cation (lanthanum) also increases the size of the boron octahedra, while the interoctahedral distances shorten. This has been attributed to the boron atoms widening their positions in order to help shield the charged interaction between neighboring cations [30].

The valence electrons of boron are distributed over five bonds. The metal atom can donate electrons to the structure, imparting a metallic character to hexaborides with metal ions having a charge greater than or equal to +3 and semiconductor characteristics to hexaborides with metal ions of lower charge. This, together with the strong bonds between the boron atoms, produces a series of compounds that have high thermal and chemical stabilities, while at the same time exhibiting unique electrochemical behavior.

It is known that when this structure is heated to a sufficiently high temperature,
<table>
<thead>
<tr>
<th>Metal</th>
<th>Lattice Constant (Å)</th>
<th>ω</th>
<th>$B$–$B_{intraO_h}$ (Å)</th>
<th>$B$–$B_{interO_h}$ (Å)</th>
<th>Ionic Radius (CN)$^i$ (Å)</th>
<th>Charge$^i$</th>
<th>Atomic Number$^i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>4.2247$^b$</td>
<td>0.1982$^b$</td>
<td>1.8033$^b$</td>
<td>1.6744$^b$</td>
<td>1.51 (8)</td>
<td>+1</td>
<td>19</td>
</tr>
<tr>
<td>Ba</td>
<td>4.2618$^c$</td>
<td>0.2046$^c$</td>
<td>1.7800$^c$</td>
<td>1.7440$^c$</td>
<td>1.42 (8)</td>
<td>+2</td>
<td>56</td>
</tr>
<tr>
<td>Sr</td>
<td>4.1953$^c$</td>
<td>0.2031$^c$</td>
<td>1.7620$^c$</td>
<td>1.7040$^c$</td>
<td>1.26 (8)</td>
<td>+2</td>
<td>38</td>
</tr>
<tr>
<td>Eu</td>
<td>4.1849$^f$</td>
<td>0.2027$^f$</td>
<td>1.7596$^f$</td>
<td>1.6964$^f$</td>
<td>1.25 (8)</td>
<td>+2</td>
<td>63</td>
</tr>
<tr>
<td>Yb</td>
<td>4.1479$^f$</td>
<td>0.2012$^f$</td>
<td>1.7525$^f$</td>
<td>1.6695$^f$</td>
<td>1.14 (8)</td>
<td>+2</td>
<td>70</td>
</tr>
<tr>
<td>Ca</td>
<td>4.1514$^c$</td>
<td>0.2019$^c$</td>
<td>1.7520$^c$</td>
<td>1.6760$^c$</td>
<td>1.12 (8)</td>
<td>+2</td>
<td>20</td>
</tr>
<tr>
<td>Sm</td>
<td>4.1346$^g$</td>
<td>0.2018$^g$</td>
<td>1.7438$^g$</td>
<td>1.6688$^g$</td>
<td>1.27 (8)</td>
<td>+2.7$^j$</td>
<td>62</td>
</tr>
<tr>
<td>La</td>
<td>4.1569$^c$ 4.1563$^d$</td>
<td>0.1995$^c$</td>
<td>1.7660$^c$</td>
<td>1.6590$^c$</td>
<td>1.16 (8)</td>
<td>+3</td>
<td>57</td>
</tr>
<tr>
<td>Ce</td>
<td>4.1407$^e$</td>
<td>0.2010$^e$</td>
<td>1.7511$^e$</td>
<td>1.6644$^e$</td>
<td>1.14 (8)</td>
<td>+3</td>
<td>58</td>
</tr>
<tr>
<td>Nd</td>
<td>4.1269$^f$</td>
<td>0.1989$^f$</td>
<td>1.7574$^f$</td>
<td>1.6415$^f$</td>
<td>1.12 (8)</td>
<td>+3</td>
<td>60</td>
</tr>
<tr>
<td>Y</td>
<td>4.1000$^c$</td>
<td>0.1988$^c$</td>
<td>1.7460$^c$</td>
<td>1.6300$^c$</td>
<td>1.02 (8)</td>
<td>+3</td>
<td>39</td>
</tr>
<tr>
<td>Th</td>
<td>4.0931$^h$</td>
<td>0.1972$^h$</td>
<td>1.7528$^h$</td>
<td>1.6143$^h$</td>
<td>1.05 (8)</td>
<td>+4</td>
<td>90</td>
</tr>
</tbody>
</table>

Table 2.2: Reported lattice constant values ($a$) and other properties for some hexaborides. References: $b = [2], c = [30], d = [83], e = [123], f = [18], g = [42], h = [72], i = [118], j = [68]$. CN = Coordination Number.

The three notable exceptions for charge determination come from the Sm, Eu, and Yb hexaborides, which typically carry a charge of +3. These anomalies are attributed to the fact that Eu and Yb form semiconductors, staying in a divalent cation (+2) state, while Sm experiences a valence fluctuation due to its 4f electron, giving a charge more appropriately given between +2.6 and +2.7, as stated by Kimura et al. [68].
the metal atoms at the surface evaporate away and are immediately replaced by diffusion of metal atoms from the underlying cells. This is supported by the fact that boron has a partial pressure of $1 \text{ Pa}$ at 2075°C, while pure lanthanum is calculated to have partial pressures almost two orders of magnitude larger [49]. During this process, the boron framework does not collapse or vaporize but remains intact [74]. In fact, the structure allows for large, apparently uncorrelated excursions of the metal ions from their equilibrium positions [121]. The migration enthalpy of a $La$ ion in $LaB_6$ has been calculated as $\Delta H_{mig} = 5.9 \text{ eV}$ [89], typical for diffusion enthalpies.

### 2.3 Mechanical Properties

Hardness is the ability of a solid to resist deformation or scratching [91]. Lanthanum hexaboride has a hardness of $\approx 9.5$, similar to $B_4C$ and between corundum ($Al_2O_3$) and diamond on the low and high ends of the Mohs scale, respectively [78]. Metal hexaborides ($M = Cr, La, Ba$) are well-known for having these high values of hardness complemented with a low density [50]. Materials with high hardness also generally share the properties of strong lattice energies and elevated melting points [91], and metal hexaborides are no exception. This makes them versatile components, as they are light-weight and can be used in applications which exploit these properties.

Compared to corundum, lanthanum hexaboride has a lower density and slightly lower bulk modulus, Young’s modulus, and shear modulus. Table 2.2 below shows some of the values of these properties for $LaB_6$ in comparison with corundum and $B_4C$ reported in the literature [78, 83].

The zero pressure bulk modulus for $LaB_6$ has been found to have values ranging from $182.4 \text{ GPa}$ to $185 \text{ GPa}$ [11, 144]. This value is fairly constant below a temperature of $200K$ after which it falls nearly linearly with temperature [50]. Between the temperature range of $0K$ and $1500K$, the drop is approximately $20\%$ [50]. This
<table>
<thead>
<tr>
<th>Property</th>
<th>$Al_2O_3$</th>
<th>$B_4C$</th>
<th>$LaB_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density ($gm/cm^3$)</td>
<td>3.89$^a$</td>
<td>2.50$^a$</td>
<td>3.77$^a$</td>
</tr>
<tr>
<td>Longitudinal Velocity (m/s)</td>
<td>10845$^a$</td>
<td>14496$^a$</td>
<td>10886$^a$</td>
</tr>
<tr>
<td>Shear Velocity (m/s)</td>
<td>6197$^a$</td>
<td>8283$^a$</td>
<td>6221$^a$</td>
</tr>
<tr>
<td>Young’s Modulus, $E$ (GPa)</td>
<td>381$^a$</td>
<td>438$^a$</td>
<td>372$^a$</td>
</tr>
<tr>
<td></td>
<td>370$^b$</td>
<td></td>
<td>376$^b$</td>
</tr>
<tr>
<td>Bulk Modulus, $B$ (GPa)</td>
<td>254$^a$</td>
<td>292$^a$</td>
<td>248$^a$</td>
</tr>
<tr>
<td>Shear Modulus, $G$ (GPa)</td>
<td>149$^a$</td>
<td>172$^a$</td>
<td>146$^a$</td>
</tr>
<tr>
<td>Debye Temperature (K)</td>
<td>1002$^a$</td>
<td>1413$^a$</td>
<td>878$^a$</td>
</tr>
</tbody>
</table>

Table 2.3: Measured mechanical properties for some hard materials. References: $a = [78]$ and $b = [83]$.

trend has been found by Gürel and Eryiğit [51] as well.

2.4 Experimental Characterization

Experimental characterization of $LaB_6$ is greatly affected by the quality of the sample. In many cases, studies are performed on samples which are inequivalent and have slightly different stoichiometric ratios of boron and lanthanum, making the task of comparison difficult [83]. Producing pure samples of $LaB_6$ is challenging and requires the correct atomic proportions and reduction in the amount of impurities within the crystal. Furthermore, the high reactivity of boron at temperatures required for synthesis presents problems [84]. Otani et. al. have used the floating zone method with $CaB_6$ as an additive to obtain stoichiometric crystals [104, 106]. Additionally, reacting a mixture of $La/Cl_2/BCl_3/H_2/Ar$ at temperatures between 1000°C and 1350°C [67], reacting lanthanum with elemental boron at temperatures over 1000°C [30], or reducing lanthanum oxides with boron carbides at $\approx 1600°C$ will produce the metal boride (along with $CO$ in the latter case) [47]. Coatings are typically
prepared by electrolytic deposition from solution or from fused molten salts [67]. Thin films from sputtering [67], vapor transport [90], evaporation [100], and chemical vapor deposition [67] have also been achieved.

The crystal structure of lanthanum hexaboride is typically determined through X-ray or neutron diffraction methods. In fact, $\text{LaB}_6$ is often used as an X-ray diffraction standard due to its narrow diffraction peaks [10, 19] and is a NIST powder diffraction reference material (NIST SRM-660a). Booth et. al. [19] have measured the average crystal structure of $\text{LaB}_6$ from the Rietveld refinement of neutron powder diffraction data (using $^{11}\text{B}$) within a temperature range of $10\, \text{K}$ to $320\, \text{K}$ and found similar values to those reported in the literature [11, 30, 34, 74, 83]. They were also able to determine the local structure through displacements generated by an X-ray absorption fine-structure (XAFS) method, finding that the separate sub-lattices of boron and lanthanum atoms are relatively uncorrelated in their vibrations.

Another difficulty that arises when experimentally characterizing the lattice structure is getting well-defined measurements of the boron network. The crystal structure typically terminates with lanthanum ions on the face, forming a $[1 \times 1]$ square lattice structure [103]. This was the speculation of Lafferty [74] more than 60 years ago and has been supported by TEM [89], low energy ion scattering [3], low energy electron diffraction (LEED) [103], angle resolved X-ray photoelectron spectroscopy (XPS) [97], and scanning tunneling microscopy (STM) data [102]. The large scattering cross sections of the lanthanum ions creates an effective barrier against electron, ion, and X-ray beams from scattering off of boron atoms, thus making analysis of the underlying boron atoms heavily reliant on extremely accurate intensity measurements [103]. Most of the information about the atomic structure on the surface is limited to lanthanum [3, 4, 97, 102], as the boron octahedra are either in the second or deeper layers, and detection is ineffective with current methodologies such as
STM and ion scattering spectroscopy (ISS) [103].

The surface structure of $LaB_6$ is not equivalent to the bulk structure [103]. Equilibrium positions of the surface lanthanum atoms have been found to relax outward slightly through high-level electronic structure methods [89]. Oshima et. al. have also determined, through a force-constant model and phenomenological analysis of surface phonon dispersions, that the top layer of boron atoms may shrink inward [103], possibly to keep the planes of the hexaboride faces normal to the lanthanum ion. Evidence for this effect was obtained by high-resolution electron energy loss spectroscopy (HREELS) [93, 94].

2.5 Electronic Properties

Electron transfer from the metal cation to the electron-deficient boron sub-lattice is the primary reason for the novel electronic properties of these materials [78]. This charge transfer between the sub-lattices results in stabilizing ionic cohesive forces between the two types of atoms to supplement the dominant B–B covalent bonds [124]. Divalent metal cations are believed to donate 2 electrons to the structure, while trivalent cations supply the required 2 electrons to saturate the boron network and therefore leave one free to roam. This spare electron provides these materials with a metallic conductivity roughly 20% of the value for copper [12, 85]. Current interest in rare-earth hexaborides is based on these ‘free’ 4$f$-electrons, which play a central role in electronic property determination [10].

Kimura et. al. have used optical conductivity spectra (obtained through reflectivity spectra transformation) to characterize the electronic properties of rare-earth hexaborides [68]. They found that below about 21 $eV$, the trivalent hexaborides spectra are all very similar to each other, speculating that this is due to the interband transition between common electronic states [68]. Up to 15 $eV$ from the Fermi
level, the occupied state is composed of the boron 2s and 2p orbitals, and the unoccupied state is composed of the rare-earth 5d state in addition to the 2s and 2p boron antibonding states [52]. Beyond this energy, the 4f state of the rare-earth metal cation modifies the structure as the orthogonalized plane-wave states dominate. The amount by which this electronic state is modified produces the interesting properties generally attributed to these compounds. As the 4f-electron number changes, the lattice constant and band structure of the rare-earth compound changes due to lanthanide contraction [68].

\[ \text{LaB}_6 \] is a typical metal with a high electrical conductivity [105] and an electrical resistivity of 6.25 \( \mu \)Ohm \cdot cm [83]. The specific resistance is approximately that of lead for well-sintered (1850°C for 30 minutes) \[ \text{LaB}_6 \] [74]. As is true for all hexaborides, the resistance-temperature coefficient is positive. The metal hexaboride with the largest specific resistance is \[ \text{CaB}_6 \] due to the cation’s small diameter [74]. Lanthanum hexaboride, which has metallic properties at room temperature, becomes a superconductor at \( T_c = 0.45 \)K [10].

The work function has been calculated for \[ \text{LaB}_6 \] as the difference between (i) the electrostatic potential of the Fermi level and (ii) the middle of a vacuum region between two symmetric slabs. Using DFT, Monnier and Delley have generated values of 2.45 eV and 2.27 eV for the unrelaxed and relaxed surfaces (described above), respectively [89]. This is in excellent agreement with experimental results from ultraviolet photoemission spectra (UPS) and HREELS [4, 97], and it is believed that the low work function can be attributed to an induced dipole on the surface atoms [103]. The relaxation at the surface forms through a redistribution of electronic charge at the surface of the slab. This creates a bonding, hybrid \( La_{1st \text{Layer}}-B_{2nd \text{Layer}} \) surface band which is \( \approx 2 \) eV below the Fermi level, as found by angular resolved UPS [5].

Thermoelectric usage of rare-earth hexaborides arises naturally from their sta-
bility and low work function. The work functions of these materials are lower than that of any known materials, with $LaB_6$ and $YB_6$ having work functions of 2.74 $eV$ and 2.22 $eV$, respectively [67]. Electron emissivity of $LaB_6$ is the highest of any compounds currently in use and it is inert with oxygen and nitrogen, giving further support for its utilization as a thermionic emitter [67]. Measured against annealed Baker’s platinum, $LaB_6$ has a thermoelectric power of 8 $\mu V/C$ over a temperature range of 100°C to 300°C [74]. Table 2.3 lists emission constants of some hexaborides for comparison.

<table>
<thead>
<tr>
<th>Boride</th>
<th>$A$ ($amps/cm^2K$)</th>
<th>$\varphi$ (volts)</th>
<th>Melting Point ($^\circ$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>2.6</td>
<td>2.86</td>
<td>2235</td>
</tr>
<tr>
<td>Sr</td>
<td>0.14</td>
<td>2.67</td>
<td>2235</td>
</tr>
<tr>
<td>Ba</td>
<td>16</td>
<td>3.45</td>
<td>2270</td>
</tr>
<tr>
<td>La</td>
<td>29</td>
<td>2.66</td>
<td>2210</td>
</tr>
<tr>
<td>Ce</td>
<td>3.6</td>
<td>2.59</td>
<td>2190</td>
</tr>
<tr>
<td>Mischmetall</td>
<td>14</td>
<td>2.64</td>
<td>—</td>
</tr>
<tr>
<td>Th</td>
<td>0.5</td>
<td>2.92</td>
<td>2195</td>
</tr>
</tbody>
</table>

Table 2.4: Hexaboride emission constants and melting points for some metals [74]. Note: Mischmetall is approximately 50% Ce, 25% La, and 25% other light lanthanides [47].

### 2.6 Thermodynamic Properties

The melting point of lanthanum hexaboride is highly variable with respect to stoichiometric composition, ranging from 2052°C to 2715°C [83]. The stoichiometric ratio ranges from $LaB_6$ to $LaB_{6.13}$, where the higher melting point is determined by the more regular $B:La$ ratio of 6:1 [83]. These ranges are due to the fact that $LaB_6$ crystallizes under non-equilibrium conditions, requiring high temperature annealing to form crystals with the proper ratio. When in use as a thermionic emitter, a
low vapor pressure caused by the boron framework complements the high melting point and allows the emitter to be heated to tens of hundreds of degrees Celsius [30].

The thermodynamic properties for lanthanum hexaboride have been the focus of many studies over the years [51], including the temperature-dependent equation-of-state, entropy ($S$), heat capacity ($C_v$), and thermal expansion coefficient ($\alpha$). These all give insight into how the crystal behaves in different environments. For instance, with the heat capacity one is able to deduce vibrational properties of the crystal at varying temperatures [50]. Using the Debye temperature, which can be thought of as the temperature at which every phonon mode is excited, one is able to extrapolate many of these thermodynamic relationships.

Most crystals, including $LaB_6$, typically follow the Debye Law for $C_v$ at low temperatures ($C_v \propto T^3$) and approach the Dulong-Petit limit for monatomic solids at higher temperatures ($C_v \approx 3R$) [50]. The problem lies in the intermediate region, which is governed by the finer details of the atomic vibrations and typically found through experiments. As no data has yet been generated for this region from experiments, Guo-Liang et al. have calculated the Debye temperature as $\theta_D = 1161.5K$ at 300K, which agrees well with calculated values of $\theta_D = 1160K$ and $\theta_D = 1000K$ at 298K from Mandrus et al. [85] and Tanaka [125], respectively. They have also found $\theta_D$ is nearly constant for temperatures lower than 150K and has an approximately linear relationship with temperature above 400K [50].

Metal hexaborides are known for having low thermal expansion coefficients [50]. The volume thermal expansion coefficient, given by

$$\alpha_V = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)$$

(2.1)

has been derived from the quasi-harmonic Debye Model with a value of $\alpha_V = 2.11 \times 10^{-5}K^{-1}$ and $\alpha_V = 2.10 \times 10^{-5}K^{-1}$ at 298K [30, 50]. This compares with diamond
(\(\alpha_V = 0.3 \times 10^{-5} K^{-1}\)), copper (\(\alpha_V = 5.01 \times 10^{-5} K^{-1}\)), and water (\(\alpha_V = 21.0 \times 10^{-5} K^{-1}\)) \[107\], for reference. The calculated \(\alpha_V\) for \(LaB_6\) agrees with values found for the linear thermal expansion coefficient (\(\alpha_L = 6.6 \times 10^{-6} K^{-1}\) (300\(K\)), 6.4 \(\times 10^{-6}\) \(K^{-1}\) (293\(K\)) \[34, 101\]), which is supposed to have the relation \(\alpha_V = 3\alpha_L\) for a cubic structure. As pressure is increased, \(\alpha_V\) decreases exponentially, and dramatically increases this trend as temperature is raised. In effect, an increase in pressure is similar to a decrease in temperature on the material \[50\].

In a study by Gürel and Eryiğit, DFT was used to extract thermodynamic data for \(LaB_6\) and \(CeB_6\) \[51\]. It has been shown by several groups that first-principles DFT treatments (within the quasi-harmonic approximation) provide a reasonable estimate to many bulk materials below their melting points \[16, 27, 108, 135\]. As \(CeB_6\) and other rare-earth hexaborides have some magnetic properties, \(LaB_6\) is typically used as the non-magnetic reference value to extract magnetism-related thermal properties of the other \(MB_6\)'s (assuming that the vibrational and electronic entropies of \(MB_6\)'s are approximately equal) \[51\]. This is done by subtracting the \(LaB_6\) entropy from the other rare-earth hexaboride entropies to obtain their respective \(S_{mag}\) values. Using this assumption, they were able to calculate the \textit{ab initio} free energy as a function of volume and performed a least-squares fit to a Vinet equation-of-state of the form

\[
E(V) = E_0 + 9B_0 V_0 \left( e^{A(1-x)(A^{-1}(1-x)-A^{-2})+A^{-2}} \right) \tag{2.2}
\]

where \(V_0\) is the equilibrium volume, \(B_0\) is the Bulk modulus, \(x = (V/V_0)^{1/3}\), \(A = 3(B'_{0} - 1)/2\), and \(B'_{0}\) is the bulk modulus pressure derivative. The overall agreement of volume thermal expansion was good for both \(LaB_6\) and \(CeB_6\) \[51\].
Chapter 3

Electronic Structure Methods

The twentieth century gave rise to a revolution in physics on the behavior of matter. Up until that point, Newton’s equations of motion and Maxwell’s relations describing electromagnetic waves were able to explain most all matters of interest. It wasn’t until Max Planck’s solution to the “UV catastrophe” originating from black body radiation and Albert Einstein’s interpretation of the photoelectric effect that physicists started to realize matter at the smallest dimensions behaved differently – energy was quantized, and the continuum theories of matter were no longer valid at these length scales.

In the 1920’s, Werner Heisenberg and Erwin Schrödinger published papers on matrix and wave mechanics, respectively, which turned out to describe this quantum world very well. Based on eigenfunctions, wave mechanics, and conservation of energy, the celebrated (time-dependent) Schrödinger equation was born [86].

\[ i\hbar \frac{\partial}{\partial t} \Psi = \hat{H} \Psi \]  

(3.1)

In this formalism, \( \Psi \) is the wave equation describing the state of the system, \( \hbar \) is Planck’s constant divided by \( 2\pi \), and \( \hat{H} \) is the Hamiltonian operator. It is Hamilto-
nian which is able to keep track of the total energy of the wavefunction, consisting of its potential ($\hat{V}$) and kinetic ($\hat{T}$) parts.

$$\hat{\mathcal{H}} = \hat{T} + \hat{V}$$

(3.2)

The concept of a wavefunction, which stemmed from the work of Louis de Broglie and his notion of “waves of matter”, allows for a probabilistic description of fundamental particles. In fact, under the interpretation of Max Born (Copenhagen Interpretation) [21], the inner product of this complex-valued vector in Hilbert space defines the probability of finding a system in a particular state. As an example, for a system composed of $N$ particles, each with locations $q_i \in \mathbb{R}^3$, $i = \{1,\ldots,N\}$, the probability of finding each particle $i$ at location $q_i$ in a volume $V_i$ is

$$P = \int_{V_1} d^3q_1 \int_{V_2} d^3q_2 \ldots \int_{V_N} d^3q_N \Psi^*(q_1,q_2,\ldots,q_N;t)\Psi(q_1,q_2,\ldots,q_N;t)$$

(3.3)

with the stipulation that the inner product is effectively normalized, as probabilities must sum to unity. Thus,

$$\int \Psi^*(q_i;t)\Psi(q_i;t)d^3q_i = \langle \Psi((q_i);t)|\Psi((q_i);t) \rangle = 1$$

(3.4)

Two simplifications to the Schrödinger equation allow it to be placed in a format which is less intractable to solve [110]. The first requires using the spectral resolution of identity, which allows for a vector in Hilbert space to be decomposed into a linear combination of orthogonal basis vectors (i.e., $\chi = \sum_k |\psi_k\rangle\langle \psi_k|\chi\rangle = \sum_k |\psi_k\rangle c_k$). If the energy of the system can be assumed constant, the Hamiltonian $\hat{\mathcal{H}}$ is invariant with respect to time. Using these two concepts, the time-independent Schrödinger equation for stationary states results.
where the time-independent wavefunction, \( \psi_j \), is derived from the temporal invariance of energy

\[
\Psi_j(\{q_i\};t) = \psi_j(\{q_i\})e^{-\frac{iE_j}{\hbar}t}
\]  

(3.6)

and the full wavefunction results from the linear combination of the basis vectors \( \Psi_j \).

\[
\Psi(\{q_i\};t) = \sum_{k=1}^{\infty} c_k \Psi_k(\{q_i\};t)
\]

(3.7)

The solution of the time-independent Schrödinger equation produces eigenvalues \( E_j \) from the eigenfunctions \( \psi_j \). These are the permitted energy levels of the stationary (or ground) states of the wavefunction, which give rise to all of the equilibrium electronic characteristics of materials. These electronic ground states determine many properties that one may not consider to be “equilibrium”, such as viscosity, diffusivity, ion conductivity, lattice vibrations, etc., as well as the typical static properties of matter like atomic structure, pressure-temperature phase diagrams, mechanical stability, and spectral functions [70]. Note that excited “electronic” states refer to matters dealing with optical properties and electronic transport.

Applications of the Schrödinger equation to real systems met with some difficulty in its early years, and further refinements were thus needed. After being published in 1926, Schrödinger’s equation was almost immediately applied to polyatomic systems and multi-electronic atoms by Heitler and London in 1927 and to solids in 1928 by Bloch [70]. However, difficulty in the solvability arose from the complicated state of nature. Matter forms a many-body system composed of atoms, each of which is interacting through Coulombic forces both intra- and interatomically between the nuclei and electrons. The two-body forces encountered from the electrostatics make
this equation inseparable and thus impractical to solve for all but a handful of ide-
alistic problems [6]. In fact, complete analytical solutions only exist for hydrogenoid
(one-electron) atoms or the $H_2^+$ molecule, and exact numerical solutions are limited
to the homogeneous electron gas, some small molecules, and atoms with few elec-
trons [70].

3.1 Adiabatic and Hartree-Fock Approximations

Starting with the complete time-dependent wavefunction of a system, various ap-
proximations have already been made in order to reduce the problem to a manage-
able size. Additional simplifications were made to further the development of a sol-
uble system. The first of these comes from the finding that the mass ratio of a single
electron to a proton is on the order 1:1836, thus making the velocities and time-
scales associated with the motion of the nuclei orders of magnitude slower than the
associated electrons [70]. In 1927, Born and Oppenheimer developed a way to justify
the separation of these two fundamental particles from the many-body wavefunction
utilizing this fact [20].

The calculation proceeded as a perturbation of the time-independent Schrödinger
equation in the mass ratio $\kappa = (m_e/M)^{1/4}$ ($m_e$ = mass of electron, $M$ = mass of nuclei),
defining a set of nuclear variables displaced from their equilibrium positions $\mathbf{R}_0$ by
a vector $\mathbf{u}$ as $\mathbf{R} = \mathbf{R}_0 + \kappa \mathbf{u}$ in order to probe the influence of the nuclear motion on the
stationary states of the electronic wavefunction. Their results from the fourth-order
perturbation suggested that no mixing of different electronic stationary states occurs
under appropriate conditions, and thus that the electrons are not likely to undergo
transitions due to nuclear interactions. In this statement, appropriate conditions
refers to the case where two or more solutions to the electronic Schrödinger equation
are energetically close [64]. The electrons essentially follow (and guide) the nuclei,
relaxing instantaneously to their ground state [62]. This is what is known as the
adiabatic theorem.

As an illustration from Kohanoff [70], we can approximate the energies of three
types of motion that a molecule can have (neglecting translation) – electronic, nu-
clear rotations, and nuclear vibrations. Electronic energies, determined by the sepa-
ration of electronic energy states, are by far the largest in magnitude. These are on
the order of the ground state energy,

\[ E_{el} \approx \frac{\hbar^2}{m_{el} a^2_{ij}} \quad (3.8) \]

with \( a_{ij} \) being the average interatomic distance. The next largest contribution comes
from vibrational energies, which can be found from the approximation of a harmonic
oscillator with frequency \( \omega \) such that \( E_v = \hbar \omega \). Assuming this frequency can be
determined from the relationships of a classical oscillator with a mass \( M_I \) and an
amplitude equal to the interatomic distances (and hence, of similar magnitude to
\( E_{el} \)), it is possible to show that \( E_{el} \approx M_I \omega^2 a^2_{ij} \), and thus

\[ E_v = \hbar \omega = E_{el} \left( \frac{m_{el}}{M_I} \right)^{1/2} \quad (3.9) \]

Nuclear rotations are related to the angular momentum of the molecules and given
by the relation \( E_r = L^2/2I \), with energy levels quantized in increments of \( \hbar \) and a
moment of inertia \( I \) on the order of \( M_I a^2_{ij} \). Setting this in terms of the electronic
energy, we have

\[ E_r \approx \frac{\hbar^2}{2M_I a^2_{ij}} \approx E_{el} \frac{m_{el}}{M_I} \quad (3.10) \]

It is easy to see here that even the largest of the nuclear energies is only a few
percent of the electronic forces, and their effect is negligible in most cases. The three
energetic relationships, in terms of $\kappa$, are

$$E_r \approx E_v \kappa^2 \approx E_{el} \kappa^4, \quad \kappa \approx \left( \frac{1}{1836} \right)^{1/4}$$ (3.11)

Another approximation, which is widely understated, is the treatment of nuclei as classical particles. They too, in fact, have their own wavefunctions and distribution over a finite space. However, two effects are sufficient to allow for neglecting this property. First, the masses of the nuclei are so great that their individual wavefunctions are heavily centered around a specific point, allowing them to be well-approximated as Dirac delta functions. Secondly, quantum phase coherence, which is a quantum effect, only becomes appreciable when the nuclear distances are less than the thermal wavelength, $\lambda_T = \frac{\hbar^2}{2Mk_B T}^{1/2}$. Again, due to the large masses of the nuclei, this interaction only becomes important at very low temperatures. Note that when the above two approximations are made, it is termed the Born-Oppenheimer approximation [70], only valid with non-degenerate electronic states [?].

Now that we have a general idea for the form of the time-independent Schrödinger equation for an electronic system parameterized by the nuclear positions, the finer details of the Hamiltonian will be discussed. As before, we can define the time-dependent Schrödinger equation as

$$i\hbar \frac{d\Psi((q_i);t)}{dt} = \hat{H}\Psi((q_i);t)$$ (3.12)

where the eigenfunctions can again be written in terms of stationary states

$$\Psi((q_i);t) = \Psi((q_i))e^{-i(E/h)t}$$ (3.13)

In the above equations, the electron intrinsic spin is assumed to be included in the spatial coordinate $q_i$ and the antisymmetry of the wavefunction with respect to
exchange of electrons, known as the Pauli exclusion principle [64], is upheld. Expectation values, which are essentially ensemble averages over the phase-space, are able to give insight into the macroscopic properties of the system. The density, for instance, is given by the density operator’s expectation value, shown here in Dirac notation (a form more suitable for matrix mechanics)

$$\hat{n}(\mathbf{q}) = \sum_{i=1}^{N} \delta(\mathbf{q} - \mathbf{q}_i) = \frac{\langle \Psi | \hat{n}(\mathbf{q}) | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$  \hspace{1cm} (3.14)

where $\delta_{ij} = 1$ for $i = j$ and $\delta_{ij} = 0$ for $i \neq j$. In the above equation, the denominator is equal to unity if the wave function is properly normalized. The Hamiltonian also has an expectation value which gives the total energy of the system. The functional form of the Hamiltonian $\hat{H}$ for electronic structure is

$$\hat{H} = \hat{T} + \hat{V}_{\text{ext}} + \hat{V}_{\text{int}} + E_{II}$$  \hspace{1cm} (3.15)

In this formalism, $\hat{T}$ is the kinetic energy operator of the electrons, $\hat{V}_{\text{ext}}$ describes the electronic field felt by the electrons due to the positively charged nuclei, $\hat{V}_{\text{int}}$ describes the electrons interacting with one another through Coulombic repulsion, and $E_{II}$ keeps track of the nuclear interactions (and possibly some other external potential). The three functionals for the electrons are defined below [86].

$$\hat{T} = \sum_i -\frac{1}{2} \nabla_i^2 \quad \hat{V}_{\text{ext}} = \sum_{i,I} V_I(|\mathbf{q}_i - \mathbf{R}_I|) \quad \hat{V}_{\text{int}} = \frac{1}{2} \sum_{i \neq j} \frac{1}{|\mathbf{q}_i - \mathbf{q}_j|}$$  \hspace{1cm} (3.16)

Coming back to the expectation value, the total energy of the system is

$$E = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \langle \hat{H} \rangle = \langle \hat{T} \rangle + \langle \hat{V}_{\text{int}} \rangle + \int d^3\mathbf{q} V_{\text{ext}}(\mathbf{q}) n(\mathbf{q}) + E_{II}$$  \hspace{1cm} (3.17)

There now exists a method for solving for the ground state wavefunction $\Psi_0$. 
Namely, this is the state with the lowest energy restricted by the constraints of particle symmetry and conservation laws. Solution of this equation can be cast in terms of the variational principle and the method of Lagrange multipliers. Supposing that there is an absolute minimum of energy, $E_0$, which could potentially be found by guessing a trial wavefunction, there is always a more accurate wavefunction to be found until the point is reached when $E_{calc} = E_0$. At this point of convergence, the exact wavefunction for the system has been found.

The Hartree-Fock method attempts to solve this problem by representing the many-body wavefunctions as a product of single-particle wavefunctions (the ansatz). Following the derivation from Martin [86], we will show the essential features of the Hartree-Fock equation. As a product of single-electron wavefunctions has no way of guaranteeing the antisymmetry conditions for exchange of identical fermions ($\langle \psi(x_1,x_2) | \psi(x_2,x_1) \rangle = 0$), the full wavefunction is expressed as the Slater determinant, $\Phi$. The rows in the Slater determinant refer to the electron coordinates and the columns correspond to single-electron wavefunctions [64]. This form has the advantage of obeying the Pauli exclusion principle and antisymmetry conditions, as the determinant of a matrix becomes zero once two columns are linearly dependent (as would be the case for two identical electrons in the same position in space) and changes sign upon interchanging of two rows (akin to switching the coordinates of two electrons) [23]. The full wavefunction becomes

$$\Phi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(q_1,\sigma_1) & \chi_1(q_2,\sigma_2) & \cdots & \chi_1(q_n,\sigma_n) \\ \chi_2(q_1,\sigma_1) & \chi_2(q_2,\sigma_2) & \cdots & \chi_2(q_n,\sigma_n) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_n(q_1,\sigma_1) & \chi_n(q_2,\sigma_2) & \cdots & \chi_n(q_n,\sigma_n) \end{vmatrix}$$

$$\langle \chi_i | \chi_j \rangle = \delta_{ij} \quad (3.18)$$
where single particle “spin-orbitals”, $\chi_i(q_j, \sigma_j)$, are just the product of functions solely dependent on the position, $\psi^\sigma_i(q_j)$, and the spin variable, $\alpha_i(\sigma_j)$. Assuming that the hamiltonian is independent of spin and spin orbitals are linearly independent, orthonormal equations, the expectation value of the energy eigenstate for the Hartree-Fock approximation can be defined as

$$
\langle \Phi | \hat{H} | \Phi \rangle = \sum_{i, \sigma} \int dq \psi^\sigma_i(q) \left( -\frac{1}{2} \nabla^2 + V_{ext}(q) \right) \psi^\sigma_i(q) + E_{II} 
$$

It is interesting to note the grouping of terms accomplished in this method. The single body terms are all encompassed in the first/single-summation term while the third and fourth two-body terms account for both direct interactions and exchanges between electrons. Note that although the third term counts the self-interaction energy of an electron in its own field, this is removed from the approximation by the exchange term, thereby getting rid of this facetious force. Solution of this system is performed using Lagrange multipliers. For spin functions which are quantized along an axis, the Hartree-Fock equations develop naturally from variation of $\psi^\sigma_i(q)$ for each spin $\sigma$:

$$
\varepsilon^\sigma_i \psi^\sigma_i(q) = \left( -\frac{1}{2} \nabla^2 + V_{ext}(q) + \sum_{j, \sigma} \int dq' \psi^\sigma_j(q') \psi^\sigma_j(q') \frac{1}{|q-q'|} \psi^\sigma_i(q) \right) \psi^\sigma_i(q) 
$$

so that the exchange term is summed over all orbitals of the same spin, again canceling out the self-interaction term.
Excellent sources on the matter [6, 64, 70, 86] and the papers by John Slater [120] and Douglas Hartree [53] can provide further explanations.

### 3.2 Density Functional Theory

DFT takes a drastic step away from the central tenet of quantum mechanics and reformulates the problem in a new light. Rather than searching the solution space for a set of $N$ wavefunctions to describe the system, it proposes that only the electron density is required to solve the state of the system. This has the effect of reducing the $3N$-dimensional problem (neglecting spin polarization) to a 3-dimensional solution, significantly reducing the cost of computation. As the system scales, and typical computations for the Hartree-Fock equations scale with $N^4$ [122], the DFT calculations are still 3-dimensional. Thus, from a computation standpoint, there are significant benefits to be had from incorporating this theory into electronic structure methods. This, among other reasons, is why DFT has become the primary tool for quantitative studies in electronic structure for condensed matter systems [40, 86].

DFT has its roots long before the modern version of the method came into being. In the 1920’s, Thomas (1927) and Fermi (1928) independently formulated the idea of utilizing electron density to calculate the energy of a system. Rather than finding the actual density of the system, their methods approximated this by way of the non-interacting homogeneous electron gas, of which good approximations were known at the time [70]. The operators for their system was based upon parameters that all depended on the density,

$$ E_\alpha[n(q)] = \int n(q)\varepsilon_\alpha[n(q)]dq $$

where the subscript $\alpha$ in this case corresponds to the origin of the contributions (i.e.
kinetic energy). This led to an equation for the Hamiltonian of the form

\[ E_{TFD}[n(q)] = C_k \int n(q)^{5/3} dq + \int n(q) v_{ext}(q) dq + \frac{1}{2} \int \int \frac{n(q)n(q')}{|q-q'|} dq dq' - C_X \int n(q)^{4/3} dq + E_C[n(q)] \]  

(3.22)

with the “D” in the subscript coming from Dirac’s (1930) contribution to the exchange energy [86]. Early attempts at using the Thomas-Fermi-Dirac model led to energies in error by 15–50% and were unable to predict actual bonding, as molecules were nonexistent in this method [70]. The approach was improved upon in the later years, but saw extreme advancement with the seminal papers from Kohn, Hohenberg, and Sham [132], who provided the basis for the use of density as the ground-state variational property and a practical procedure for execution of these calculations.

### 3.2.1 Hohenberg-Kohn Theorems

Hohenberg and Kohn laid the foundation for treating the electron density as the primary variable for the electronic structure calculations. Their 1964 paper provided two theorems which allowed one to switch focus from the wavefunction mentality. These are summarized below [59]:

1. For a collection of an arbitrary number of electrons under the influence of an external potential \( v_{ext}(q) \) and mutual Coulomb repulsion, the potential \( v_{ext}(q) \) is, to within a constant, uniquely determined by the ground-state density \( n_0(q) \).

2. There is a universal functional \( F[n(q)] = \langle \Psi | \mathcal{T} + \mathcal{V} | \Psi \rangle \) valid for any number of particles and any external potential \( v_{ext}(q) \) which gives the correct ground-state energy of the system when minimized, and the density obtained by doing so is the ground-state energy density \( n_0(q) \).

Proof of these theorems is carried out by a reductio ad absurdum argument and
can be found in many texts on the subject, including the original paper by Pierre Hohenberg and Walter Kohn [59]. In short, the results lead to an equation of the form

$$E_v[n(q)] = \int v_{ext}(q)n(q)dq + F[n(q)]$$  \hspace{1cm} (3.23)$$

with the operator $F[n(q)]$ being the sum of the Hartree term and another universal functional, $G[n(q)]$, which incorporates the effects due to exchange, correlation, and the kinetic energy.

$$F[n(q)] = \frac{1}{2} \int \frac{n(q)n(q')}{|q-q'|}dq dq' + G[n(q)]$$  \hspace{1cm} (3.24)$$

Now we move on to determination of this functional.

### 3.2.2 The Kohn-Sham Ansatz

The approach developed by Kohn and Sham in 1965 replaces the many-body interacting system with a different auxiliary system formed from independent particles and an interacting density, leading to exactly soluble independent particle equations for the non-interacting system [86]. The basis for their formulation came as a modification to the Hohenberg-Kohn theorem (Lu Sham was a post-doc working with Kohn at the time [60]). They were able to construct a form for the $G[n(q)]$ functional as

$$G[n(q)] \equiv T_s[n(q)] + E_{xc}[n(q)]$$  \hspace{1cm} (3.25)$$

with $T_s[n(q)]$ being the kinetic energy of a system of non-interacting electrons and $E_{xc}[n(q)]$ representing the many-body effects (i.e., exchange and correlation) for an interacting system [71]. Applying the variational principle to both the non-
interacting and the interacting systems, one finds

\[ \delta E_v[n(q)] \equiv \left\{ v_{\text{ext}}(q) + \frac{\delta T_s[n(q)]}{\delta n(q)} \right\} \delta n(q) = 0 \]  

(3.26)

and

\[ \delta E_v[n(q)] \equiv \left\{ v_{\text{ext}}(q) + \int \frac{n(q')}{|q-q'|} dq' + \frac{\delta E_{xc}[n(q)]}{\delta n(q)} + \frac{\delta T_s[n(q)]}{\delta n(q)} \right\} \delta n(q) = 0 \]  

(3.27)

Replacing \( v_{\text{ext}}(q) \) with \( v_{\text{eff}}(q) \), one is left with the following self-consistent equations

\[ \left\{ -\frac{\hbar^2}{2m} + v_{\text{eff}}(q) - \epsilon_j \right\} \psi_j = 0 \]  

(3.28)

\[ v_{\text{eff}}(q) = v_{\text{ext}}(q) + \int \frac{n(q')}{|q-q'|} dq' + v_{xc}(q) \]  

(3.29)

\[ n(q) = \sum_{1}^{N} |\psi(q)| \]  

(3.30)

\[ v_{xc}(q) \equiv \frac{\delta E_{xc}}{\delta n(q)} \]  

(3.31)

to be solved iteratively, beginning with a trial-density, assuming an exchange energy \( E_{xc} \), solving for \( v_{\text{eff}}(q) \), and then recalculating \( n(q) \) until convergence is achieved [60].

### 3.3 Periodic Potentials

So far, we have described methods for determining the electronic structure of a system by making alterations and approximations to the Hamiltonian operator. The next set of approximations to be made deal with the actual geometry of electrons in space and the argument to the functional, namely, the electronic wavefunctions. Before we get into that, we will briefly discuss some of the finer points of simulating periodic systems, as these give rise to a whole new set of approximations. In gen-
eral, these only truly valid for a perfect lattice (pure and without defects), but most crystals can be approximated in such a way with minimal error [6].

The Bravais lattice which describes a crystal is periodic in nature, meaning that the unit cell repeats in a regular array in all directions. This leads one to believe that the electrons which are prescribed to every atom should each experience the same environment as its image in neighboring cells. Assuming $U(q)$ is the potential, this can be described as

$$U(q + R) = U(q)$$

(3.32)

with $R$ being a linear combination of the primitive lattice vectors. Since the potential describes the force acted upon by the electrons, this also implies that the ground state wavefunctions inside of each crystal are identical in each cell and respect the translational periodicity of the crystal [70]. This has important consequences, leading to Bloch’s theorem.

### 3.3.1 Bloch’s Theorem

Considering again a crystal, these macroscopic objects can contain on the order of $10^{23}$ atoms, repeated in all directions of the primitive lattice vectors. What Bloch’s theorem allows one to do is to connect the properties of an electron in an infinite periodic system with those of the unit cell [70]. As previously stated, the potential in a crystal lattice can be assumed to vary periodically from cell to cell. Thus, one can write the one-electron wavefunction as the product of a function with an identical periodicity as the potential along with an imaginary phase factor (which handles the translational symmetry) [6], such that it follows the Born-von Karman boundary conditions,

$$\psi_k = e^{ik \cdot q} u_k(q) \quad \text{with} \quad u_k(q) = u_k(q + a_i)$$

(3.33)
with \( \mathbf{k} \) being the crystal momentum vectors in reciprocal space. Displacing the wavefunction by a unit vector \( \mathbf{R} \) produces

\[
\psi_k(\mathbf{q} + \mathbf{R}) = e^{i\mathbf{k} \cdot \mathbf{R}} \psi_k(\mathbf{q})
\]

(3.34)

for every \( \mathbf{R} \) resulting from the Bravais lattice. Note that this phase factor drops out when one finds the probability distribution [70].

\[
\langle e^{i\mathbf{k} \cdot \mathbf{R}} \psi_k(\mathbf{q}) | e^{i\mathbf{k} \cdot \mathbf{R}} \psi_k(\mathbf{q}) \rangle = |\psi_k(\mathbf{q})|^2
\]

(3.35)

The periodicity also implies specified values for the momentum vectors \( \mathbf{k} \). The phase factor must have the following relationship

\[
e^{i\mathbf{k} \cdot \mathbf{R}} = e^{2\pi i} = 1 \quad \forall \quad \mathbf{k}
\]

(3.36)

This restricts the values of \( \mathbf{k} \) to the reciprocal lattice vectors \( \mathbf{G} \), further reducing the complexity of the solution technique. For reference, the reciprocal lattice is defined by its relationship to the primitive vectors \( (\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3) \) of the direct lattice [6]

\[
\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)} \quad \mathbf{b}_2 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)} \quad \mathbf{b}_3 = 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}
\]

(3.37)

### 3.3.2 Brillouin Zone Sampling & Irreducible Brillouin Zones

The Brillouin zones are volumes in reciprocal space segregated by the bisecting Bragg planes of the reciprocal lattice [86]. They are ordered by their distance from the origin, with the first Brillouin zone defined as the volume originating from the origin and ending on the first Bragg plane. This specific Brillouin zone is synonymous with the Wigner-Seitz primitive cell in the reciprocal space, with a volume of...
\( V_{BZ} = \frac{(2\pi)\Omega}{2}, \) making it the smallest repeating unit constructed from the \( k \)-points.

The second Brillouin zone is the volume outside of the first Brillouin zone ending on the next Bragg plane it meets, and so on [6].

According to Bloch’s theorem, it is sufficient to only determine the electronic wavefunctions within the unit cell, as the neighboring cells will only differ by a phase factor \( e^{ik \cdot a} \) [70]. However, the calculation for the all-electron wavefunction in the infinite solid will be mapped to the wavefunction in the first Brillouin zone for a finite number of electrons and, in principle, requiring an infinite number of \( k \) vectors. In practice, this is done only using a finite number of \( k \)-points in the first Brillouin zone, though this value depends on various features of the system and the properties desired [69, 70].

Symmetrical features of the lattice structure allow for reductions in the number of \( k \)-points. Combinations of point symmetries (reflections, rotations, and inversions) and translations leave the system invariant and commute with the Hamiltonian for periodic systems [86]. It can be shown that symmetric \( R_i \) and translational \( t_i \) operations on the wavefunction

\[
\psi_{R_i}^{k}(R_iq + t_i) = \psi_{i}^{k}(q) \quad \psi_{R_i}^{-1}^{k}(q) = \psi_{i}^{k}(R_iq + t_i)
\]  

(3.38)

are also eigenfunctions of the Hamiltonian producing in the same \( \epsilon_i^k \). This result allows us to define what’s known as the irreducible Brillouin zone (IBZ), which is the smallest portion of the Brillouin zone containing all of the necessary information for electronic structure calculations. The use of the IBZ can have drastic roles in reduction of the number of \( k \)-points to sample, requiring only \( 1/48^{th} \) of the full Brillouin zone for high symmetry cubic crystals [86].

The choice of \( k \)-points can also have a dramatic effect on the efficiency of the computation. A widely used scheme taken advantage of in this research is that de-
veloped by Monkhorst and Pack in 1976 [70]. The Monkhorst-Pack grid is applicable to all symmetries and well-developed for metallic systems, which require an even finer sampling to capture the shape of the Fermi surface. The general algorithm generates a set of \( k \)-points from a linear combination of the reciprocal lattice vectors with the coefficients determined by a set of natural numbers ending with a value \( q \).

\[
k = n_1 b_1 + n_2 b_2 + n_3 b_3 \quad n_i = \frac{2r - q - 1}{2q} \quad r = 1, 2, \ldots, q
\] (3.39)

### 3.4 Plane-Wave Basis Sets

The method of electronic structure calculations involves mapping the atomic orbitals onto molecular orbitals using a finite number of basis functions, which are ideally functions that mimic the actual orbitals [64]. When dealing with periodic systems, an appropriate basis set used is composed of a number of plane-waves, as they have many attractive features for describing these systems. One of these pertains to the solution of electronic structure for condensed phases, which requires that they do not violate Bloch’s theorem, implying periodicity. For wavefunctions to be correct solutions, they must have a phase factor and a periodic part with frequencies relative to the lattice vectors [70]. Plane-waves adhere to this condition naturally, and give rise to the solution of the Schrödinger equation in the presence of a constant external potential [70]. However, as one moves closer toward the nuclei, the potential becomes dramatically different so a linear combination of increasing numbers of plane-waves is thus required. Other reasons for this choice of basis are that plane-waves are mutually orthogonal, they agree fairly well with the physics, are easily calculated using fast Fourier transforms, and tend to converge as more basis functions are added [86]. These are all properties which follow the guidelines given by Jensen [64].

It is instructive to see how plane-waves fit into this picture. A Fourier transform
(in reciprocal space) of a function is written as

\[ u_k(q) = \int e^{i\mathbf{g} \cdot \mathbf{q}} \tilde{u}_k(g) dg \]  

(3.40)

Using Bloch’s theorem, the values of \( g \) for the above function are restricted to the the reciprocal lattice vector \( \mathbf{G} \). Thus, the general expression for this type of wavefunction is

\[ \psi^k(q) = \frac{e^{ik\mathbf{q}}}{\sqrt{\Omega}} \sum_{G=0}^{\infty} C_k(G)e^{iG \cdot q} \]  

(3.41)

with the plane-wave basis functions (with \( \Omega \) being the volume of the primitive cell) described as

\[ \phi_G(q) = \frac{1}{\sqrt{\Omega}} e^{iG \cdot q} \]  

(3.42)

following the normalization and orthogonalization properties

\[ \langle \phi_G | \phi_{G'} \rangle = \frac{1}{\Omega} \int_{\Omega} e^{i(G-G') \cdot q} dq = \frac{1}{\Omega} (\Omega \delta_{G,G'}) = \delta_{G,G'} \]  

(3.43)

This results in the wavefunction for different eigenstates \( j \)

\[ \psi^k_j(q) = e^{ik \mathbf{q}} \sum_{G=0}^{\infty} C_{jk} \phi_G(q) \]  

(3.44)

### 3.5 Pseudopotentials

The concept of the pseudopotential dates back to the work of Hans Hellman in 1935 who had developed an effective potential for valence electron scattering from metallic ion cores. These potentials ended up being too hard, however, and perturbation methods at the time did not allow for accurate calculations [86]. Soon after, Slater (1937) and Herring (1940) proposed models using augmented plane-wave expansions with spherical solutions to the atomic problem (APW, augmented plane-wave
method) and linear combinations of plane-wave and core wavefunctions for valence wavefunctions (OPW, orthogonalized plane-wave method), respectively [70]. For appropriate choices of the expansion coefficients in the OPW method, the wavefunctions became orthogonal to the core states, and the use of core orbitals drastically reduced the number of plane-wave components needed for valence-state reproduction. These advances led to more developments and the origin of the modern pseudopotential method in the familiar paper from Philips and Kleinmann in 1959 [109]. These authors added on to the OPW method by forming equations for the valence electrons depending on a weaker/softer effective potential [86].

The problem of the core electron wavefunctions has already been alluded to in the description of plane-wave basis sets. In order to combat the use of larger and larger basis-sets, the strong Coulomb potential of the nucleus and the core electrons (those not participating in any relevant chemistry) are replaced by an effective ionic potential which acts on the valence electrons [86]. Thus, the core states are effectively fixed in an atomic reference configuration (frozen core approximation) and the ground state pseudo-wavefunction identically mimics the all-electron wavefunction outside of the core cut-off radius [119]. Fitting of the pseudopotentials is generally accomplished by comparison to all-electron wavefunctions, with the advantage of reducing the number of electrons, electronic states, and basis sets to be considered, and therefore the calculation expense [70].

3.5.1 Norm-Conserving

Two general types of pseudopotentials exist for electronic structure calculations. The first one developed is the norm-conserving pseudopotential and has its roots in many fundamental ideas relating to physical considerations. The norm-conserving pseudopotentials rest on the following ideas [86]:
1. All-electron and pseudo-valence eigenvalues agree for chosen atomic reference states.

2. All-electron and pseudo-valence wavefunctions agree beyond a chosen core radius, $R_c$.

3. Pseudo wavefunction and all-electron wavefunction logarithmic derivatives agree at the point $R_c$.

4. The integrated charge for each wavefunction agrees inside $R_c$ (the “norm-conserving” condition).

5. The first energy derivative of the log derivatives of both wavefunctions agree at $R_c$.

These properties have the effect of producing a transferable wavefunction with an accurate charge-density and is the reason for their popularity and continued use in research today [119]. The drawback to the norm-conserving potentials is that in order to have a pseudopotential which has a high accuracy and transferability, a low cut-off radius was required (creating a “hard” potential). However, computational considerations lead one to desire the least amount of basis sets (cost scales as a power of the number of Fourier components required) producing smooth curves which are inherently linked to larger cut-off radii [86].

3.5.2 Ultrasoft

The problems encountered with norm-conserving pseudopotentials are their hardness and high energy cut-off values. To alleviate this complication, Vanderbilt (1990) suggested an alternative whereby the norm-conserving constraint was relaxed, allowing for softer potentials with a large reduction in the energy cut-off values [119]. This became the foundation for ultrasoft pseudopotentials. The softness of these potentials is linked to their use of fewer basis sets, re-expressing the problem in terms
of a smooth function and an auxiliary function localized around the core to represent the rapidly varying region of the density, allowing for larger cut-off radii [86]. To compensate for the difference in charge density (as it is a function of the wavefunction), an additional term is added in the calculation to produce the correct results from the all-electron wavefunctions [70]. Substantial reductions in the energy cut-offs for plane-wave calculations have been acquired by Koval et. al. in simulating oxygen with ultrasoft potentials, producing the same level of accuracy with a decreased energy cut-off value from 150 $R\gamma$ to 40 $R\gamma$ [73].

### 3.6 Potential Energy Surface

With the basic tools of quantum mechanics in hand, one should understand that a given spatial arrangement of nuclei will give rise to varying levels of energy eigenstates. If one were to map out the potential energy as a function of some spatial distribution of nuclear coordinates, a hypersurface would result, showing how the potential energy changes as one samples the space of all possible geometric coordinates [110] – this is the concept of a potential energy surface (PES). The first of such surfaces were formulated well before the advent of computers, by Henry Eyring and Michael Polanyi in 1931 to describe the transition of a proton through an activated complex, ultimately leading to the celebrated transition-state theory [81]. A fully characterized PES is a function of all of the degrees of freedom a particular set of nuclei have, showing all possible conformations and rearrangements and their relationship to the system's potential energy [35].

Within the Born-Oppenheimer approximation, it is valid to assume that the nuclei are effectively “swimming” in a sea of electron density, their motions restricted by the hypersurface on which they lie. The adjustment of the electrons is considered to be so fast that, neglecting relativistic effects, nuclei almost behave like ball
bearings on a smoothly varying terrain. This type of notion represents one of the most important ideas in chemistry [110], as it allows one to locate both ground and transition-state structures through analysis of a PES [35]. As the atoms gain momentum through collective motions and thermal energy, they are stimulated to traverse low-energy paths to find new local minima, otherwise known as chemical reactions.

In connection with calculus, the extreme values of a function are related to the local and global maxima and minima. In order to distinguish between the two sub-types, a further analysis with second derivatives will typically lead one to the conclusion of where it lies in relation to its surroundings. These critical points are of great practical importance to chemistry when considering the PES [35]. The local minimum of energy corresponding to the molecules equilibrium structure is found at the point where the gradient with respect to all coordinates (or degrees of freedom) is zero and the Hessian matrix is positive for all deviations [81], signifying that the molecule has found itself in a basin. If thermal energy isn’t large enough for the molecule to escape a well, then a stationary state has been found. For reference, the elements of the Hessian matrix are defined by [8]

\[ H_{ij} = \frac{\partial^2 E}{\partial q_i \partial q_j} \] (3.45)

Another particularly interesting location on the PES is again characterized by a vanishing gradient and positive second derivatives, with the exception that the components of the Hessian are negative for one, and only one, coordinate [8]. This can be graphically depicted as a saddle point, and it is well-known that trajectories traveled by this single coordinate represent the lowest energy path between two states [35]. These low energy barriers give rise to the most favorable and probable directions for a molecule to reach another valley on the hypersurface. The trip taken
by the particle is intimately related to the transition-structure or path.

As an example of the transition state between two configurations, consider ion diffusion within the lanthanum hexaboride system. The most favorable position for a $\text{La}$ ion is at the equilibrium position. However, ionic diffusion is known to occur within these frameworks. Using DFT, we can calculate the evolution of the energy as an ion travels through the boron framework along the minimum energy path. Two curves are shown, one representing the lattice at its calculated equilibrium structure and the other for a constricted system (lattice constant reduced by 14%). Thus, as $\text{La}$ ions receive enough energy they are able to overcome the activation energy and “hop” between the barriers (assuming the nearest neighbor cell is empty). This is depicted below in Fig. 3.1 (note that the actual system may have a slightly different relationship, since the hexaboride units were held fixed during the simulation).

### 3.6.1 Geometry Optimization

Being certain the correct geometry has been located is an important task in computational chemistry, as one needs to know whether the structure they are dealing with is an actual observable of nature. Equilibrium structures are those with minima of the energy, as nature tends to minimize (free) energy at all costs [35]. A typical starting point in the geometry optimization process is to use suitable molecular geometry that is believed to resemble the desired stationary point [81]. Experimental or $\text{ab initio}$ structures are good examples of initial configurations.

The next step in the optimization process is to systematically change the positions of the atoms in such a way that the energy decreases until a critical point is achieved [8]. Typical methods for optimization involve sophisticated iterative differential techniques employing either the gradient or both the gradient and Hessian of the energy with respect to coordinates in order to determine the direction of down-
Equilibrium structure was found through geometry optimization of both lattice constant and crystallographic refinement parameter $\omega$ (defined in Chapter 2). The constrained lattice used the same relative lattice distances with a lattice constant value 86% the size of the equilibrium length, effectively shrinking the system. Energy values are reported relative to the energy difference observed for the equilibrium structure. Total energy values for the equilibrium and constrained structures were -6786.9 eV and -6742.8 eV, respectively. The $\Delta H_{mig}$ for the equilibrium structure was found to be 9.144 eV, 55% higher than the DFT calculated value of Monnier et. al [89] (perhaps due to the inability of the boron sub-lattice to accommodate fluctuations or the exclusion of holes/empty cells).
ward slope for sampling [81]. Partial derivatives are numerically determined and the Hessian (which is an \( N \times N \)-matrix) is generally approximated in a similar manner [35]. The ‘line search’ and Newton-Raphson methods are two examples of these approaches [35].

In the case of lanthanum hexaboride, we have calculated the energy changes with respect to lattice constant and crystallographic refinement parameter \( \omega \). A close-up look at the optimization can be seen in Fig. 3.2, where both \( \omega \) and \( a \) have been optimized to create the lowest energy structure. The lattice energy for a set of lattice constants at the optimal \( \omega \) is shown below in Fig. 3.3. As we can see, there is initially a steep decrease in energy related to the electronic exchange energy overlap producing atomic repulsion. As we move further along increased lattice constants, the potential energy decreases until it reaches a minimum at the local optimum structure (gradient is zero and Hessian is positive). This is shown as Point B in the figure. A combination of favorable electrostatic and van der Waals forces act to keep the crystal in this specific coordinate of phase-space. Stretching the bonds further reduces these favorable contacts between electron clouds, so the potential energy is again increased and reaches a fairly constant value.
Figure 3.2: DFT results for $\text{LaB}_6$ structure optimization.
Lattice energies at various values for $a$ and $\omega$ are shown near the equilibrium geometry. Structural optimization is seen at $\omega = 0.2001$ and $a = 4.154\,\text{Å}$. 
Figure 3.3: Variations in $\text{LaB}_6$ lattice energy for optimal $\omega$.
Unit cell with crystallographic refinement parameter ($\omega = 0.2001$) is stretched equally along all three coordinate axes. The minimum energy on this one-dimensional PES corresponds to the equilibrium structure. *Point A*: Electron cloud overlap and strong repulsive forces; *Point B*: Local equilibrium structure at the bottom of the energy basin, *Point C*: Molecular system is stretched far enough that favorable electron overlap is no longer observed and atoms begin to behave similar to an isolated state.
Chapter 4

Classical Atomistic Modeling

The modeling of atomic systems has come a long way since the advent of modern computational techniques for simulation. Prior to the introduction of these tools, large assemblies of macroscopic spheres were typically used to simulate condensed systems (e.g., dense liquids) [1]. These models could, depending on the “potential” desired, be constructed from either metal ball bearings or gelatinous spheres to represent the molecules, being kept in motion by mechanical vibration [1, 41]. Remarkably, these models displayed some realistic behavior considering their crude construction, though analysis of results required one to resort to using a computer [41].

The first simulation to be carried out by a computer on a dense liquid (composed of 2-dimensional hard spheres) was performed by Metropolis, Rosenbluth, Rosenbluth, Teller, and Teller at Los Alamos National Laboratory in 1953 [41]. This computer, the MANIAC, was the most powerful computer at the time, and their work helped to lay the foundation for modern Monte Carlo methods used today [1]. Since then, many ground-breaking simulations have been run. A selection of these is given below in Table 4.1.

It is very surprising to see how important molecular models and simulations have become in all facets of science. Rather than being used simply for calculations,
<table>
<thead>
<tr>
<th>Year</th>
<th>Authors</th>
<th>Simulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1953</td>
<td>Metropolis et al</td>
<td>MC simulation of hard spheres</td>
</tr>
<tr>
<td>1955</td>
<td>Fermi, Pasta, Ulam</td>
<td>MD of anharmonic, 1-D crystal</td>
</tr>
<tr>
<td>1956</td>
<td>Alder, Wainwright</td>
<td>MD of assembly of hard spheres</td>
</tr>
<tr>
<td>1957</td>
<td>Wood, Parker</td>
<td>MC simulation of LJ potential</td>
</tr>
<tr>
<td>1959</td>
<td>Vineyard et al</td>
<td>Radiation damage in crystalline copper</td>
</tr>
<tr>
<td>1964</td>
<td>Rahman</td>
<td>MD of liquid argon (LJ potential)</td>
</tr>
<tr>
<td>1968</td>
<td>Harp, Berne</td>
<td>MD of diatomic molecular liquid</td>
</tr>
<tr>
<td>1969</td>
<td>Berker, Watts</td>
<td>MC simulation of liquid water</td>
</tr>
<tr>
<td>1971</td>
<td>Rahman, Stillinger</td>
<td>MD of liquid water</td>
</tr>
<tr>
<td>1973</td>
<td>Barojas, Levesque, Quentrec</td>
<td>MD of rigid diatomic molecules</td>
</tr>
<tr>
<td>1975</td>
<td>Ryckaert, Bellemans</td>
<td>MD of liquid n-butane</td>
</tr>
<tr>
<td>1977</td>
<td>McCammon, Gelin, Karplus</td>
<td>MD of folded proteins</td>
</tr>
</tbody>
</table>

Table 4.1: Some pioneering achievements of molecular simulation [1, 41]. MC = Monte Carlo, MD = Molecular Dynamics, LJ = Lennard-Jones.

The computer has become a ‘virtual laboratory’ in which to conduct numerical experiments [113]. In fact, it is becoming increasingly rare that any new theories are applied without prior testing on a computational platform. Well-devised simulations can give insight into the physics of the problem as well as produce preliminary results [41]. This has the potential to rule out a large number of actual experiments that need to be carried out in order to achieve success, drastically cutting costs and time required.

MD has even approached the limit of utilizing either all or part of a quantum mechanics result in simulations. Various schemes involve either a hybridized framework, in which the bulk of the simulation is carried out by MD and only a particular site is modeled via quantum mechanics, to the fully quantum \textit{ab initio} MD (examples are Ehrenfest Molecular Dynamics, Born-Oppenheimer Molecular Dynamics, and Car-Parrinello Molecular Dynamics) [48]. As computers become faster and al-
Algorithms allow for greater speeds, larger and more complex simulations will continually be within the reach of an eager scientist.

4.1 Molecular Dynamics Principles

In the most simplest sense, MD allows for the time-evolution of a system guided by the deterministic features of classical mechanics. For those who are familiar with Laplace's demon, it suffices to say that the computer acts as the "intelligence which could comprehend all the forces by which nature is animated and the respective situation of the beings who compose it" [76]. Thus, the laws of classical (Newtonian) mechanics are applied to a system composed of either bonded or non-bonded molecules and atoms, each of which has a definite position and velocity in phase-space and is acted upon by a conservative force generated by its interaction with each of the other particles in the system [13]. In this respect, 'classical' refers to the fact that nuclear motions obey the laws of classical mechanics [41]. The potentials are typically spherically symmetric functions based upon exotic springs [113] which interact between pairs of atoms, derived from experiment or the electronic ground-state structure of the time-independent Schrödinger equation [13]. Quantum effects are generally excluded, only being necessary when considering the translational and rotational motion of light atoms and molecules or vibrations with a frequency $\hbar \nu > k_B T$ [35].

The use of simple potentials has succeeded in reproducing many important qualitative and quantitative features of atomic and molecular systems, though there is always room for improvement. A full calculation of all the interactions of the system will give rise to a PES, along which the molecules will travel with varying momenta dictated by their respective thermal kinetic energies [64]. This surface requires a simple description to be able to treat the motion of molecules in large systems over reasonable time spans, so simpler models are preferred in that regard [13].
Classical MD involves the solution of Hamilton’s equations of motion

\[ \dot{q}_i = \frac{\partial H}{\partial p_i} \quad \dot{p}_i = -\frac{\partial H}{\partial q_i} \] (4.1)

where the canonical coordinates \( q_i \) and \( p_i \) refer to the position and velocity of particle \( i \) and the Hamiltonian \( H \) is the total energy of the system [14]. In many cases, Cartesian coordinates \( q_i \) and velocities \( v_i (p_i/m_i) \) are used. For conservative force fields with no external potentials, the force is a function of only the coordinates and derived from the total potential acting on a particular particle.

\[ H(p_i, q_i) = \sum_i \frac{p_i^2}{2m_i} + E(q_i) \] (4.2)

\[ v_i = \dot{q}_i \] (4.3)

\[ F_i = -\frac{\partial}{\partial q_i} E(q_i) = m_i \ddot{v}_i = m_i \ddot{q}_i \] (4.4)

We will see later that the velocity becomes a non-essential feature in some circumstances for temporal evolution of trajectories, since the force (and thus acceleration) is only dependent on coordinates [14].

As one may have guessed, there are many approximations made in the solution of these equations, as the accuracy of numerical integration is only one of the factors which govern the precision. In this regard, we should understand that the goal of MD is not to be able to predict the exact trajectory of a system given a specific initial configuration in phase space. In fact, systems with very similar starting trajectories invariably will diverge exponentially from true trajectories, a symptom known as the Lyapunov instability [41]. Hence, the interest in MD is the extraction of statistical predictions, averaging out the noise to relate relevant data to an initial configuration for which something is known (e.g., total energy) [41].
There are a vast number of ways that MD is put to use to produce useful information. Some of these involve simulating systems for which data is readily available (a good way to check that models are accurate); others include exploiting its capability to produce results for which no experiment has been performed or the conditions of which make it intractable to give reliable results. One can think of these simulations as an extension of real-world experiments – a sample is prepared by selecting a model system, equilibrated so that wild fluctuations are depressed, and then measurements are taken [41]. Take note of the similarities between this algorithm and how actual experiments are conducted. Once equilibration has been achieved within the simulation, fundamental studies on phenomena (such as phase transitions, diffusion, transport properties, dielectric properties, fluid dynamics, etc.) can be performed on systems ranging from complex fluids to solids to biomolecules [113]. The possibilities are virtually limitless, and computational power is only increasing.

4.1.1 Ensembles

Statistical mechanics allows one to connect the macroscopic properties of a system to the fundamental behavior of its constituent molecules [126]. When a measurement is made on a macroscopic property, the value obtained is due to chaotic motions of a large number of molecules, giving rise to high frequency fluctuations [111]. Thus, observed properties are determined by the time-averages of this dynamical state of the system [56]. For a property $A$, this may be written as

$$\langle A_{obs} \rangle = \frac{1}{\tau} \int_{t_0}^{t_0 + \tau} A(p, q) dt$$

(4.5)

where $\tau$ is the duration of the measurement. In classical statistical mechanics, this type of computation is impossible for real systems with $\approx 10^{23}$ degrees of freedom, and we utilize the ensemble method of Gibbs for averaging over states [56]. The
connection to MD should be clear within this formulation – modeling a macroscopic system in terms its particles and their interactions over a collection of states.

There are two fundamental postulates [57] to statistical mechanics which will be of use to this discussion. These are:

1. The (long) time average of a mechanical variable $M$ in the thermodynamic system of interest is equal to the ensemble average of $M$, in the limit as $\mathcal{N} \to \infty$, provided that the systems of the ensemble replicate the thermodynamic state and environment of the actual system of interest (ergodic hypothesis).

2. In an ensemble ($\mathcal{N} \to \infty$) representative of an isolated thermodynamic system, the systems of the ensemble are distributed uniformly, that is, with equal probability or frequency, over the possible quantum states consistent with the specified values of $N$, $V$, and $\mathcal{E}$.

The notion of an ensemble and its usage can be illustrated through the description of the canonical ensemble from Hill [56, 57]. Imagine there are a large number $\mathcal{N}$ of independent systems, each with the same fixed volume ($V$), number of particles ($N$), and temperature ($T$). For this, suppose that the total system is isolated and composed of the ensemble and an infinite heat bath at temperature, $T$. There are a number of energy states available to these independent systems, and, at any point in time, $n_i$ systems will be have energy $E_i$. Conservation laws require that

$$\sum_i n_i = \mathcal{N}$$ \hspace{1cm} (4.6)

$$\sum_i n_i E_i = \mathcal{E}_{\text{total}}$$ \hspace{1cm} (4.7)

Assuming that these can be arranged in any order within the macroscopic isolated system, the total number of states which can be observed by this distribution is given...
by the multinomial distribution:

\[
\Omega_t(n) = \frac{(\sum_i n_i)!}{\prod_i n_i!}
\] (4.8)

The probability of observing a given quantum state, \(E_i\), taking into account the second postulate, is given by the ratio of its average value and the total number of states:

\[
P_i = \frac{n_i}{\mathcal{N}} = \frac{1}{\mathcal{N}} \frac{\Omega_t(n)n_i(n)}{\sum_n \Omega_t(n)}
\] (4.9)

Recognizing the application of the central-limit-theorem and law of large numbers in this case (\(\mathcal{N} \to \infty\)), we are able to replace the probability of \(n_i\) with its value in the most probable distribution, \(n_i^*\), as all other terms will be negligible.

\[
P_i = \frac{n_i^*}{\mathcal{N}} = \frac{1}{\mathcal{N}} \frac{\Omega_t(n_i^*)n_i^*}{\Omega_t(n_i^*)}
\] (4.10)

In order to find the value \(n_i^*\), we need to maximize \(\Omega_t(n_i^*)\) subject to the conservation equations. Using the Lagrange method of undetermined multipliers with Eqn. (4.6) and Eqn. (4.7) as constraints, we take Stirling’s approximation (using the logarithm of the multiplicity for numerical convenience) and differentiate,

\[
\frac{\partial}{\partial n_i} \left[ \ln \Omega_t(n) - \alpha \sum_j n_j - \beta \sum_j n_j E_j \right] = 0, \quad i = 1, 2, \ldots
\] (4.11)

to obtain

\[
e^\alpha = \sum_i e^{-\beta E_i}
\] (4.12)

\[
\bar{E} = \frac{\sum_i E_i e^{-\beta E_i}}{\sum_i e^{-\beta E_i}}
\] (4.13)

where the partition function is given by
\[ Q = \sum_i e^{-\beta E_i} \] (4.14)

It is a trivial task to show that \( \beta = (k_B T)^{-1} \) and correlate it to the entropy, and many references can be found which do so [56, 57, 111, 126]. The relevant point about this derivation is that we have obtained the average value of the internal energy and the partition function for a particular ensemble. As is known from thermodynamics, the Helmholtz free energy is described by the same conditions as the canonical ensemble [126]. It can be shown, through some simple operations, that the Helmholtz energy is connected to the partition function by [57]

\[ A(N, V, T) = -k_B T \ln Q(N, V, T) \] (4.15)

from which all other properties in this system can be calculated utilizing the derivative relations of thermodynamics [126].

Other ensembles can be solved in a similar manner, either through the use of the canonical ensemble or with different constraints. These are listed in Table 4.2. Implementation of these specific ensembles in a dynamics simulation can be set up using various algorithms to control environmental and internal variables.

<table>
<thead>
<tr>
<th>Name</th>
<th>Fixed Variables</th>
<th>Thermodynamic Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>Canonical</td>
<td>( N, V, T )</td>
<td>Helmholtz Free Energy</td>
</tr>
<tr>
<td>Microcanonical</td>
<td>( N, V, E )</td>
<td>Internal Energy</td>
</tr>
<tr>
<td>Grand Canonical</td>
<td>( \mu, V, T )</td>
<td>No Analog</td>
</tr>
<tr>
<td>Isothermal-Isobaric</td>
<td>( N, P, T )</td>
<td>Gibbs Free Energy</td>
</tr>
<tr>
<td>Isoenthalpic-Isobaric</td>
<td>( N, P, H )</td>
<td>No Analog</td>
</tr>
</tbody>
</table>

Table 4.2: Common ensembles found in MD simulations [28, 126].

Extraction of data from a simulation follows directly from the ideas of statistical
mechanics. Rather than using the ensemble averages, however, we have data from
time-dependent evaluations of the energies, coordinates, and velocities involved. Ta-
Table 4.3 shows some of these quantities which can be easily calculated.

<table>
<thead>
<tr>
<th>Average Quantity</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kinetic Energy</td>
<td>$\frac{1}{2} \left\langle \sum_i m_i (v_i(t))^2 \right\rangle$</td>
</tr>
<tr>
<td>Temperature</td>
<td>$\frac{1}{N_{DOF} \cdot k_B} \left\langle \sum_{i=1}^{N} m_i (v_i(t))^2 \right\rangle$</td>
</tr>
<tr>
<td>Pressure</td>
<td>$\left\langle \frac{N k_B T}{V} + \frac{1}{3V} \sum_{i=1}^{N} \sum_{j&gt;i} N_{ij} \cdot F_{ij} \right\rangle$</td>
</tr>
<tr>
<td>Mean-Square Displacement</td>
<td>$\left\langle</td>
</tr>
<tr>
<td>Diffusivity</td>
<td>$\lim_{t \to \infty} \frac{1}{6t} \left\langle</td>
</tr>
</tbody>
</table>

Table 4.3: Relationships to derive thermodynamic quantities from molecular dynam-
ics results of 3-dimensional systems [41, 126].
Note that $\left\langle A \right\rangle$ refers to the time average of quantity $A$; $N_{DOF} =$ degrees of freedom.

Now that we have a good description of the thermodynamics of the system, some
practical aspects of implementation will be reviewed.

4.1.2 Boundary Conditions

The size of a system is one of the factors which contribute to the length of simulation
time, as computations involving pairwise interactions must be performed on every
set of atoms within a specified cut-off radius. In addition, surface effects will play
an important role on modest-sized simulations, as a system with $N$ particles will
generally have on the order of $N^{2/3}$ particles near the walls [113]. For example, a
simulation in a cubic box with 1000 particles will have close to 500 of these particles
near the surface. Rather than increasing the size (and thus computation time), other schemes have been devised to eliminate the wall-effects and allow for the simulation of systems which are larger than one can afford to simulate [13].

Methods to treat the boundary conditions include the use of periodic boundary conditions, continuum boundary conditions (which utilize some kind of reflecting wall), and restrained-shells (for use with solvated proteins) [13]. Due to their simplicity, popularity, and applicability to crystal lattices, periodic boundary conditions will be of use for this study [13, 28]. To understand the general idea of periodic boundaries, imagine a three-dimensional rectangular box with a single particle. As the particle moves through the box and eventually reaches an edge, it is allowed to pass through the edge and return through the opposite side rather than be reflected. Thus, a particle passing through the top face will re-enter the bottom face with the same velocity. Another way to think about this is through the mapping of a two-dimensional system onto a torus [113]. This sort of transformation allows the system to be exactly replicated in all directions, giving rise to a periodic lattice constructed from one unit cell [13]. Rectangular cells are not the only type to be considered, and other lattices constructed from any space-filling, convex region can be tailored to one’s experimental framework, whether it be to decrease the surface to volume ratio (e.g., truncated octahedron) or model crystalline solids with non-orthogonal axes (e.g., trigonal unit cell) [113].

In practice, the unit cell is better described as a supercell, constructing a few repeated structures of the primitive cell in order to reduce simulation noise. As will be discussed, some forces are more easily handled through the use of a cut-off radius, which essentially truncates the potential at the specified distance. Restrictions involving the cut-off radius require that its value be no more than half of the smallest length of the periodic cell. This is needed in order to remove the possibility of spuri-
ous self-interactions, and typical cut-off values are generally much smaller [113].

Other considerations to the use of periodic boundaries involve long-range inter-
actions, such as electrostatic interactions (described by the Coulomb potential) and
long-range motions of neighboring cells [13]. Electrostatics do not handle well with
truncations and require special treatment [113]. The long-range motion of neighboring
cells is invariably suppressed due to the periodic nature, such that all phenomena
involving $k$-vectors in reciprocal space which are not multiples of the reciprocal
basis vectors are absent (implying periodic nature in potential functions) [13]. Thus,
small system sizes should be avoided to minimize these effects.

### 4.1.3 Equilibration

Any MD method should always begin with an equilibration of the system. This has
very important consequences related to debugging and ensuring that the system is
in a stable state. In this equilibration step, the simulation is allowed to run for a
period of time using the initial lattice configuration [1]. Velocities are prescribed
random directions and a fixed set of magnitudes dictated by a desired temperature,
and the particles are placed on the lattice corresponding to a specific density [113].
The system should reach an equilibrium state, allowing a Maxwell-Boltzmann dis-
tribution of velocities and equipartition of energy [28].

To be sure that an equilibrated state has been found, the potential energy and
pressure of the system can be monitored [1]. It is not unusual for these values
to drift in the initial stages, as the potentials (which can be thought of as springs)
can give rise to extremely large forces if the atoms lie in a region where electron
clouds overlap [113]. Equilibration can be considered complete once the pressure and
energy terms have oscillatory behavior around mean values and the systematic drift
is quenched [1]. Another useful feature for solids is analysis of the mean-squared
displacements of atoms about their initial lattice positions [1]. A production run can then be implemented if the oscillations are well-behaved, allowing analysis of dynamical and structural features of the system [28].

Before we dive in to the finer details of integrating the equations of motion, it is helpful to briefly discuss some properties which make a simulation algorithm successful. Speed and accuracy are competing factors in this respect, as we would like to have a simulation that requires less simulation time (larger time steps), but only at the expense of marginal decrease in accuracy [1]. The computation of the force is by far the most laborious task, taking as much as 97% of the total CPU time, and must be completed at every interval [14, 28, 41]. In this respect, it is advisable to use methods which only require one force evaluation per step, ruling out the well-known Runge-Kutta methods (which usually require 4 evaluations) [13, 14]. As Newton’s equations of motion are time-reversible, the algorithm should be as well, in addition to having a symplectic property (i.e., the ability to conserve volume in phase-space —see [77] for a detailed exposition on the importance of symplectic properties in integration schemes) [1, 13, 41]. The higher-order predictor-corrector algorithms, which have seen wide use in MD, do not follow these guidelines, having serious long-term energy drift problems, and thus will only merit this brief mention [41]. The Verlet-style algorithms, which are of low-order, have been shown to have moderate short-term energy conservation and produce very little long-term drift [41].

Other factors which contribute to a successful algorithm are low memory requirements, satisfaction of conservation laws, simple form, magnitude of global and local truncation errors, and being well-behaved for the forces encountered [1, 14]. However, a trade-off must be made when considering all aspects. Higher-order schemes allow for larger time steps at the expense of storing increasingly higher-order derivatives of the particle coordinates [13]. These schemes generally have very good en-
ergy conservation for short times, but lead to erroneous results and overall energy drifts for larger simulation lengths [13]. In practice, the total energy is not exactly conserved due to integration errors, truncation of forces, and finite precision of the calculations, allowing for an infinitessimal perturbation to grow exponentially [13, 64, 113]. Analysis of the PES's from MD simulations has shown that the second derivatives with respect to most coordinates are positive, suggesting that the algorithm should at least include a proper treatment of third-order terms to avoid instability and accumulation of errors in the solution, though extension beyond these terms is generally not advantageous for complex systems with force truncation [14].

The final thing to consider is the step length used. This is of critical importance, as it must be smaller than the time-scale of the fastest processes occurring; typically any important dynamic atomic or molecular processes are taken into account [28, 64]. Molecular motions, such as rotations and vibrations, generally have frequencies $\omega$ between $10^{11} - 10^{14}$ Hz, so that time steps on the order of femtoseconds or less (one would typically reduce the length of the fastest motion by at least a factor of 10) are required to allow for a decent compromise between speed and accuracy [28, 64]. Constraints which fix these motions can give rise to unacceptable errors and are not advised [64].

Computational speed can also be increased by the inclusion of truncated forces, especially for non-ionic systems containing only short-ranged forces. The use of a cut-off radius can reduce the summation of pairwise interactions from $\mathcal{O}(N^2)$ to $\mathcal{O}(N)$ [28]. Neighbor-lists, which are implemented in most simulations today, keep track of all molecules within a spherical shell of radius slightly larger than the cut-off value and further increase speeds, as the state space does not have to be continually searched for neighbors which fall inside the truncated region [1, 28, 113]. These lists are typically updated once every 10 to 20 time-steps to ensure continued
accuracy [1].

4.2 Integration Schemes

4.2.1 Euler Methods

Methods of integration referred to as Euler methods attempt to find the future trajectories in phase space through a simple Taylor expansion of the particle positions [1]. In its most general form, the Taylor series for a function \( f(x) \) about a point \( a \) can be written as

\[
f(x) \approx \sum_{n=0}^{\infty} \frac{f^{(n)}(a)}{n!}(x-a)^n
\]  

(4.16)

where it is assumed that the function is differentiable at the point \( a \). Euler methods truncate the expansion after the second derivative of the particles position, giving

\[
q(t + \Delta t) = q(t) + v(t)\Delta t + O(\Delta t^2)
\]  

(4.17)

\[
v(t + \Delta t) = v(t) + a(t)\Delta t + O(\Delta t^2)
\]  

(4.18)

\[
a(t) = \frac{F(q)}{m}
\]  

(4.19)

It has been shown that this procedure will not generate accurate trajectories as time advances and the behavior of the function is not well-suited for MD applications [1, 14]. In addition, the algorithm is neither symplectic nor time-reversible and suffers a catastrophic energetic drift [41]. This, however, sets the stage for better approximations to be considered next.
4.2.2 Verlet-Type Algorithms

Moving on to more accurate and robust methods, we will begin with the Verlet algorithm and then show the modifications made in order to produce the two integration schemes employed by DL_POLY_4. The Verlet algorithm, which was adopted by Verlet in 1967, involves the direct solution of the second-order equations $m_i \ddot{q}_i = F_i$ [1]. The derivation is simple enough, utilizing forward and reverse Taylor series approximations about the point $q(t)$.

\[
q(t + \Delta t) = q(t) + v(t)\Delta t + a(t)\frac{\Delta t^2}{2} + b(t)\frac{\Delta t^3}{6} + \mathcal{O}(\Delta t^4) \tag{4.20}
\]

\[
q(t - \Delta t) = q(t) - v(t)\Delta t + a(t)\frac{\Delta t^2}{2} - b(t)\frac{\Delta t^3}{6} + \mathcal{O}(\Delta t^4) \tag{4.21}
\]

Addition of the previous two equations yields the Verlet integrator with error in particle coordinates of order $\mathcal{O}(\Delta t^4)$ [113].

\[
q(t + \Delta t) = 2q(t) - q(t - \Delta t) + a(t)\frac{\Delta t^2}{2} + \mathcal{O}(\Delta t^4) \tag{4.22}
\]

Noting that the velocities are not determined in the formulation, these must be computed in retrospect by [1]

\[
v(t) = \frac{q(t + \Delta t) - q(t - \Delta t)}{2\Delta t} + \mathcal{O}(\Delta t^2) \tag{4.23}
\]

as they are needed to evaluate the kinetic energy of the system. This set-back can sometimes have detrimental effects when trying to connect a system with an ensemble for a desired temperature setting [64].

The Verlet algorithm has the advantage of being time-reversal (since properly centered positions play symmetrical roles), symplectic, fast, requires about as little memory as possible, produces little long-term drift, and has only modest short-term
energy conservation properties \cite{1,41}. Disadvantages of the algorithm stem from its calculation of new positions and lack of information about the current velocity distribution \cite{64}. As can be seen from the above equations, the evolution of the particle trajectories relies on the addition of a small value, $a(t)\Delta t^2$, to the difference of the two relatively large values of the positions, $q(t)$ and $q(t-\Delta t)$, which can become problematic due to finite numerical accuracy \cite{64}. The lack of a proper inclusion of the velocity into the equations of motion also limits the use of this method with techniques that scale kinetic properties (in application of the canonical ensemble, for instance).

The Leap-Frog algorithm attempts to correct some of the deficiencies in the Verlet method, namely the awkward handling of the of the velocities and the summation of terms with very different orders of magnitude (one with $O(\Delta t^2)$ and the other with $O(\Delta t^0)$) \cite{1}. In order to counteract these problems, the velocites are instead computed at the midpoints of the temporal evolution of the system and then resubmitted back into the solution of the trajectory \cite{13}. This simple mechanism of “hopping” between time-steps gives rise to the name, and the adjustment to the equations of motion not only reduces errors, but allows for kinetic coupling \cite{1}. The derivation of the Leap-Frog algorithm also stems from the Taylor series expansion as follows \cite{113}:

\begin{equation}
q(t + \Delta t) = q(t) + v(t)\Delta t + a(t)\frac{\Delta t^2}{2} + O(\Delta t^3) \tag{4.24}
\end{equation}

Utilizing the following expansion of the velocity and rearranging the initial Taylor expansion, we find:

\begin{equation}
v\left(t + \frac{\Delta t}{2}\right) = v(t) + a(t)\frac{\Delta t}{2} + O(\Delta t^2) \tag{4.25}
\end{equation}

\begin{equation}
q(t + \Delta t) = q(t) + \left(v(t) + a(t)\frac{\Delta t}{2}\right)\Delta t + O(\Delta t^3) \tag{4.26}
\end{equation}

Inclusion of Eqn. (4.25) into Eqn. (4.26) produces the Leap-Frog scheme. It can be
shown by simple algebra that the error in the coordinate is of order \( \mathcal{O}(\Delta t^3) \) while the velocities are still of order \( \mathcal{O}(\Delta t^2) \).

\[
\mathbf{q}(t + \Delta t) = \mathbf{q}(t) + \mathbf{v}\left(t + \frac{\Delta t}{2}\right) \Delta t + \mathcal{O}(\Delta t^3)
\]

The velocities for half-integer time-steps are then determined by

\[
\mathbf{v}\left(t + \frac{\Delta t}{2}\right) = \mathbf{v}\left(t - \frac{\Delta t}{2}\right) + \mathbf{a}(t) \Delta t
\]

Two methods have been found which estimate the velocities at the proper time, which either take the geometric average of the forward and reverse velocities [1, 13, 14, 28] or utilize a truncated Taylor series for a step length of \( \frac{1}{2} \Delta t \) [113].

\[
\mathbf{v}(t) = \frac{1}{2} \left\{ \mathbf{v}\left(t + \frac{\Delta t}{2}\right) + \mathbf{v}\left(t - \frac{\Delta t}{2}\right) \right\}
\]

\[
\mathbf{v}(t) = \mathbf{v}\left(t - \frac{\Delta t}{2}\right) + \mathbf{a}(t) \Delta t
\]

The stored quantities in this algorithm are minimal and consist of the current positions \( \mathbf{q}(t) \), accelerations \( \mathbf{a}(t) \), and mid-step velocities \( \mathbf{v}(t - \frac{\Delta t}{2}) \) [1]. This type of method is preferred over the Runge-Kutta integration schemes owing to their time-reversibility and improved energy conservation, and tend to work better when simulating Lennard-Jones potentials [64, 113].

The Velocity-Verlet algorithm is the final integration scheme to be covered. This method has gained popularity due to its successful computation of both velocities and trajectories at the same point in time [41]. There are two stages involved in the calculation, with a force evaluation placed in between [1]. In the first iteration,
positions \( q(t + \Delta t) \) are calculated from [13]

\[
q(t + \Delta t) = q(t) + v(t)\Delta t + a(t)\frac{\Delta t^2}{2}
\] (4.31)

and midpoint velocities are found from

\[
v\left(t + \frac{\Delta t}{2}\right) = v(t) + a(t)\frac{\Delta t}{2}
\] (4.32)

The force is then computed using trajectories at \( q(t + \Delta t) \), followed by the second velocity advancement.

\[
v(t + \Delta t) = v\left(t + \frac{\Delta t}{2}\right) + a(t + \Delta t)\frac{\Delta t}{2}
\] (4.33)

This method uses 9\( N \) words of storage to fully carry out an iteration, but the numerical stability, convenience, and simplicity make it one of the most attractive integration schemes proposed to date [1]. One thing to note is that all methods based on the Verlet algorithm have identical global errors and generate precisely the same trajectories – they are only algebraic reformulations of the same equation [1]. However, they do produce different system energies, as the kinetic energy component is evaluated at a different time (also allowing for some to be coupled to external degrees of freedom) [41].

On a final note, some methods for checking the accuracy of simulations will be discussed. First off is that conservation laws should be properly obeyed, allowing for constant energy [1]. The constancy of the total and kinetic energies and their standard deviations must always be tested, decreasing the time-step as the first step in troubleshooting if either of these values drift [28]. A good guess for a time-step is on the order of 10 \( fs \), though crystals containing light particles will need
to be integrated on the order of 1 fs intervals to properly capture the physics \[28\]. For Lennard-Jones systems, fluctuations on the order of \(10^{-4}\) are considered acceptable \[1\]. Before performing a full-length production run, several short runs should be performed with different time steps, equalling the same total time, and each run analyzed on the basis of RMS fluctuations. These should be proportional to \(\Delta t^2\) for Verlet algorithms if the program is functioning correctly \[1\].

### 4.2.3 Temperature and Pressure Control

Standard MD implementations generate a system within the microcanonical ensemble, keeping the energy constant and allowing temperature and pressure to fluctuate \[64\]. It is desirable in some cases to carry out simulations on systems which are typically encountered in real-world experiments. Modifications to the Hamiltonian can be performed in order keep certain properties of the system constant \[14\]. This is achieved by way of feedback mechanisms, which allow one to scale variables to produce the correct value for the property \[41\]. As an example, we know that the temperature is directly related to the kinetic energy of the system \((T_{av} \propto v_{av}^2)\), so a proper rescaling of the velocities will encourage the system to fluctuate around a selected temperature. Similar methods apply to pressure control with coordinate and/or velocity scaling \[13\].

Many methods are available for rescaling purposes, most of which are related in some form to the Langevin equation \[63\].

\[
a(t) = \frac{F(t)}{m} - \gamma(t)v(t) + \frac{R(t)}{m} \tag{4.34}
\]

Four general classes of altering the Hamiltonian are given below, along with a specific method developed. \[13, 61, 63\]

1. **Stochastic Methods** Frictional forces and stochastic forces are applied so
that rescaling of the momentum has the form $\dot{p}_i = F_i - \gamma p_i + R_i(t)$ (Langevin thermostat/barostat) or particles are selected at random and reassigned a velocity according to a Maxwell-Boltzmann distribution for the desired temperature (Andersen thermostat).

2. **Weak-Coupling Methods** A perturbation to the system with a first-order rate equation is added to smoothly reduce variables to a preset value through a coupling constant $\tau$. The property $X$ is rescaled by $\frac{\delta X}{\delta t} = (X_{desired} - X)/\tau_x$ (Berendsen thermostat/barostat).

3. **Strong-Coupling Methods** Directly rescales the velocities at every time-step by enforcing that $\delta E_{kin}/\delta t = 0$ (Evans-Hoover thermostat).

4. **Extended-System Dynamics** Addition of a dynamic particle with its own “mass” (in units of $J/s^2$) and velocity, which acts as an external heat bath to rescale the variables, producing a new Hamiltonian to encapsulate the extended system. Deviations from the desired value of the system property affect the velocity of the dynamic particle (leading to second-order control), which scales the actual system’s variables (Nosé-Hoover thermostat/barostat).

In choosing a correct thermostat or barostat to use, one needs take into account the time-reversibility, ensemble generated, dynamical properties, and limitations of the method. Only the Nosé-Hoover and Evans-Hoover methods are time-reversible, and the three algorithms that produce a canonical distribution of microstates and configurations are the Langevin, Andersen, and Nosé-Hoover stats [63]. Thus, it is no surprise that Nosé-Hoover thermostats and barostats are widely used in MD simulations. The only apparent detractor to this method is its oscillatory behavior due to the second-order coupling from the scaling factor [13]. In order to avoid large systematic fluctuations, equilibration should be handled with an approach that has a smooth exponential decay (such as a Langevin or weak-coupling method) before applying Nosé-Hoover [13].
4.3 Force Fields

Interactions between and within molecules are most accurately computed via the \textit{ab initio} methods described earlier, providing a solution to the Schrödinger equation. However, simulations of dynamical properties require very short time-steps and large system sizes in order to produce accurate results. If one is faithfully trying to model dynamics in a fully quantum framework, the length of CPU time and/or amount of computing power needed to extract reliable data for any reasonable amount of simulated time becomes prohibitive \cite{110}. Thus, simplifications are made to these interactions to produce force fields which govern the effects of a molecule in its environment.

The two most notable simplifications inherent in most force fields are the decoupling of the rotational and vibrational degrees of freedom \cite{110} and the assumption that the information contained in the electronic (ground-state) structure can be subsumed into a truncated series of analytical interatomic potentials \cite{28}. Regarding the decoupling of the vibrational and rotational motion, an elementary understanding of physics will show that a rotating body produces a centrifugal force which would act to extend bond lengths, with the two energies related through the radial distance and moment of inertia, $I = \mu R^2$ \cite{110}. A third, but important fact to note, is that charge polarization is generally not handled in most force fields employed, as they require iterative minimization techniques for each progression and therefore decrease computational efficiency \cite{35}.

Under the classical assumption, we have already seen how we can advance a molecular system through space and time once the potential is known. This potential energy is typically written in a similar format to the power series, adding up all of
the terms involving interactions of single particles, pairs, triplets, etc. [28]

$$E_{total}(q_1, q_2, \ldots, q_N) = \sum_{i=1}^{N} \phi_1(q_i) + \sum_{i=1}^{N} \sum_{j>i}^{N} \phi_2(q_i, q_j) + \sum_{i=1}^{N} \sum_{j>i}^{N} \sum_{k>j}^{N} \phi_3(q_i, q_j, q_k) + \cdots \quad (4.35)$$

where the first term $\phi_1$ is related to the energy of the molecules in their isolated states and, if applicable, under the influence of some kind of external field. The summations following take into account two-body, three-body, and higher-order interactions between the particles. Aside from bonded interactions, it is customary to only include the pairwise interactions in force fields for simulations due to economical reasons as these scale on the order of $\mathcal{O}(N^2)$ and are generally sufficient to capture a majority of the physics, assuming the force fields have been properly parameterized (including all three-body interactions adds $\mathcal{O}(N^3)$) [1]. This turns out to be a surprisingly good approximation for ionic crystals, where the majority of interactions are non-directional [28]. Since the resulting pairwise molecular potentials incorporate many-body interactions, they are often denoted “effective pair-potentials” [35].

In order to further simplify the force field, we assume the potentials can be expanded in terms of the effects which they reproduce within the system, taking note that some of these are multi-body interactions [64]:

$$E_{force\ field} = E_{stretch} + E_{bend} + E_{torsion} + E_{cross} + E_{vdW} + E_{elec} \quad (4.36)$$

The foundation of this assumption is based on the simple observation of the similarities in the structural units of molecules. For example, all $C-H$ bond lengths tend to be roughly the same value, implying that the force constants between carbon and hydrogen are similar as well [64].
4.3.1 Non-Bonded Interactions

The intermolecular forces stem from interactions between atoms (or rather, electrons and protons) which are not covalently bonded to one-another. These are dependent on the separation \( r_{ij} = |q_i - q_j| \) between two atoms or molecules, varying in strength as one moves through a range of distances [66]. Although many of these interactions are not explicitly accounted for in the force field model, a proper parameterization will include these to some extent [28, 64]. Note that computation of these interactions is the most time-consuming part of a simulation.

Starting from zero separation of the molecules, strong repulsive forces are observed. They can be attributed to the unfavorable (non-bonding) overlap of the molecular electronic shells such that electronic exchange energy repels the two atoms [66]. Alternate interpretations invoke the Pauli exclusion principle [80] and the strong Coulombic forces between like-charged electrons at such short distances [64]. From electronic structure theory, it is known that this force has the approximate form of

\[
E_{rep}(r_{ij}) \approx f(r_{ij})e^{-\alpha r_{ij}}
\]  

(4.37)

However, complex calculations such as exponentials, square roots, and trigonometric functions take \( \approx 5 \) times as long to compute, so most implementations of this force utilize a function proportional to the inverse of some even power of \( r_{ij} \) to circumvent these issues [64].

As the atoms move further away, the electronic exchange repulsion decreases and attractive forces begin to dominate [66]. It is in this region where ionic bonding, condensation, and solidification occur. Neglecting electric monopoles, the various forces which have favorable interactions are related to the polarization of the electronic clouds surrounding the molecules to lower the energy and promote attraction. These
are commonly referred to as induction forces (dipole-induced dipole), London dispersion forces (induced dipole-induced dipole), and various other multipole-multipole interactions [111]. A well-known form of dipole-dipole interactions is the common hydrogen bond, and this tends to be the strongest of the non-bonded interactions if present (due to the 3-center 4-electron bonds typically formed) [7, 35]. These forces generally have distance- and polarity-dependence of the potential proportional to

$$E_{pol}(r_{ij}) = \frac{1}{r_{ij}^{n_{p,i}+n_{p,j}-1}}$$

(4.38)

where $n_{p,i}$ is essentially the number of vectors required to describe the charge-separated poles on each molecule “$i$” [7]. Also, for clarity, it should be noted that dipole-dipole interactions are extremely variant on the angle/geometry between the two poles. Thus, when averaged out over all possible conformations (in the case of disordered media), these give rise to the Keesom force proportional to $r^{-6}$ [7].

Before considering monopolar interactions, it is worthwhile to note that the form of the non-bonded forces typically have only three terms – repulsion, attraction, and electrostatic. Therefore, each of the polarized terms considered thus far is generally lumped into one potential, the van der Waals force.

The final type of interatomic interaction stems from the strong electronic nature of monopoles. These can be either monopole-monopole (Coulombic/electrostatic) forces or between monopoles and various other multipoles (ion-dipole) [111]. Assuming the ion-dipole moment is absorbed into one of the two interatomic forces, the electrostatic potential varies with distance proportional to $r_{ij}^{-1}$ [54]. This makes them the strongest and longest-ranged of the non-bonded potentials, and is one of the reasons the non-bonded force calculation requires the most effort. The other factor which proves these to be cumbersome is their convergence, which will be discussed later.
A typical form of the non-bonded interactions includes the repulsion, van der Waals, and electrostatic terms, and these are depicted below in Fig. 4.1.

\[ E_{\text{non\_bonded}}(r_{ij}) = \frac{A_{ij}^{\text{rep}}}{r_{ij}^n} - \frac{B_{ij}^{\text{vdW}}}{r_{ij}^m} - \frac{C_{ij}^{\text{el}}}{r_{ij}} \]  

(4.39)

Figure 4.1: Examples of non-bonded interactions (arbitrary units).
*Top left:* repulsive potential, *top right:* van der Waals type attractive potential, *bottom left:* electrostatic potential, *bottom right:* total non-bonded potential.

### 4.3.2 Bonded Interactions

The interactions between atoms within the same molecule present a much simpler problem for computation, though proper parameterization may be tricky. The four
most commonly used types of interactions are bond stretching, angle bending, bond torsion, and the cross-coupling term [81]. The potentials describing these terms can be placed in a very general framework with the help of two operations: (1) setting the potential energy to zero at its minimum value (2) and performing a Taylor series approximation about the natural/equilibrium value of the variable involved [64]. In this manner, we can write the contributions to the potential energy changes arising from variations of an ambiguous characteristic as [35]

$$
\begin{align*}
E_{\text{bond}}(\mathbf{q}) &= E(\mathbf{q})|_{\mathbf{q}=\mathbf{q}_{eq}} + \sum_{i=1}^{N_{DOF}} (\Delta q_{i,eq}) \frac{\partial E_{\text{bond}}(\mathbf{q})}{\partial q_i}|_{\mathbf{q}=\mathbf{q}_{eq}} \\
&\quad+ \frac{1}{2!} \sum_{i=1}^{N_{DOF}} \sum_{j=1}^{N_{DOF}} (\Delta q_{i,eq})(\Delta q_{j,eq}) \frac{\partial^2 E_{\text{bond}}(\mathbf{q})}{\partial q_i \partial q_j}|_{\mathbf{q}=\mathbf{q}_{eq}} + \cdots \quad (4.40)
\end{align*}
$$

where $\Delta q_{i,eq}$ represents deviations from the equilibrium value of this variable. A consideration of calculus allows us to conclude that the first two terms are zero, producing

$$
E_{\text{bond}}(\mathbf{q}) = \frac{1}{2} \sum_{i=1}^{N_{DOF}} \sum_{j=1}^{N_{DOF}} (\Delta q_{i,eq})(\Delta q_{j,eq}) \frac{\partial^2 E_{\text{bond}}(\mathbf{q})}{\partial q_i \partial q_j}|_{\mathbf{q}=\mathbf{q}_{eq}} + \cdots \quad (4.41)
$$

If only the harmonics are kept, these represent a linear set of spring equations (Hooke’s Law), with spring constants dictated by the second derivatives [116]. Note that all of the second-order diagonal ($i = j$) terms represent potentials for the same interaction, and the off-diagonal terms represent mixed/cross interactions. Corrections for anharmonicity can be accounted for by adding further terms to the Taylor expansion or utilization of a more exact representation [64].

### 4.3.2.1 Bond Stretch

The stretch energy describes the deviation of the potential energy associated with bond vibrations in covalently bonded systems [28]. The harmonic potential is gener-
ally a good approximation when the force constant $k_{AB}$ is high or the bond isn’t required deviate too large from its equilibrium value [35]. If better approximations are needed to reproduce the vibrational frequencies, or the system is highly strained, anharmonic terms of the Taylor series to the third or fourth powers can be used, though these tend to lose accuracy and diverge with increased separations [64]. Use of more realistic functions such as the Morse potential can be implemented if bond-breaking is desired (with the caveat of decreased efficiency from the exponential term) [110]. However, systems rarely acquire these energies, so a polynomial expansion is typically sufficient for most applications [116]. A typical bond stretching potential has the form

$$E_{\text{stretch}}(\Delta r_{AB,eq}) = \frac{1}{2} \left[ k_{AB} + k_{AB}^{(3)}(\Delta r_{AB,eq}) + k_{AB}^{(4)}(\Delta r_{AB,eq})^2 \right] (\Delta r_{AB,eq})^2$$

(4.42)

where higher-order terms are kept as necessary.

### 4.3.2.2 Angle Bending

For a triatomic atom or section of an atom $A - B - C$, distortions in the angle $\theta_{ABC}$ connecting fragments $A - B$ and $B - C$ lead to steric increases in energy [81]. These can again be approximated with the harmonic potential, using higher-order terms to improve fits over a wider range and for strongly deformed angles [64, 116]. Vibrational spectroscopy has even shown that associating the potential with a polynomial expansion provides good fits to data for small displacements, though no power expansion will show the correct behavior as the bonds become linear or for molecules with multiple angular minima [35]. The form typically adopted only contains second-order terms, but for completeness, we write

$$E_{\text{bend}}(\Delta \theta_{ABC,eq}) = \frac{1}{2} \left[ k_{ABC} + k_{ABC}^{(3)}(\Delta \theta_{ABC,eq}) + k_{ABC}^{(4)}(\Delta \theta_{ABC,eq})^2 \right] (\Delta \theta_{ABC,eq})^2$$

(4.43)
with $\theta_{ABC}$ given by

$$\theta_{ABC} = \arccos \frac{\mathbf{r}_{AB} \cdot \mathbf{r}_{CD}}{r_{AB}r_{BC}} \quad (4.44)$$

### 4.3.2.3 Torsion

Torsion is a four-atom effect and relates the torque resulting from the twisting motion about the $B - C$ bond in an $A - B - C - D$ fragment. It is especially useful in modeling systems which have a planar nature due to $\pi$-bonding or gauche interactions from interactions of bulky ligands [28]. As the bond has a full $360^\circ$ periodicity, this interaction is best modeled as a summation of trigonometric functions based on the dihedral angle $\omega_{ABCD}$ formed between the $A - B$ and $C - D$ fragments [64].

$$E_{\text{torsion}}(\omega_{ABCD}) = \sum_{n=1} K_n \cos(n\omega_{ABCD}) \quad (4.45)$$

with $\omega_{ABCD}$ found by

$$\omega_{ABCD} = \arccos \frac{\mathbf{r}_{BA} \times \mathbf{r}_{CA} \cdot \mathbf{r}_{CB} \times \mathbf{r}_{DB}}{||\mathbf{r}_{BA} \times \mathbf{r}_{CA}|| ||\mathbf{r}_{CB} \times \mathbf{r}_{DB}||} \quad (4.46)$$

The values of $n$ given in Eqn. (4.45) relate to the periodicity of the cosine function such that $n = 1$ implies $2\pi$ periodicity, $n = 2$ allows for the interaction to be periodic in $\pi$, etc.

### 4.3.2.4 Cross-Coupling

Considering the case of a water molecule, it would make sense that as the two hydrogens are bent inward, the bond lengths increase to reduce the steric repulsion. This type of coupling hasn’t yet been implemented as the stretch and bend terms are uncorrelated and no account is made to handle van der Waals interactions intramolecularly. To cope with this problem, cross-coupling parameters have been
developed [110]. The functions to describe this effect are the off-diagonal terms in the Taylor series approximation made for the intramolecular bonding in Eqn. (4.40). Two of these are shown below for clarification.

\[ E_{\text{bend/stretch}}(\Delta r_{AB,eq}, \Delta \theta_{ABC,eq}) = \frac{k_{AB,ABC}}{2} (\Delta r_{AB,eq})(\Delta \theta_{ABC,eq}) \]  

\[ E_{\text{stretch/stretch}}(\Delta r_{AB,eq}, \Delta r_{BC,eq}) = \frac{k_{AB,BC}}{2} (\Delta r_{AB,eq})(\Delta r_{BC,eq}) \]  

In addition to avoiding intramolecular van der Waals forces, relationships such as the stretch-stretch term are especially important for modeling \( \pi \)-conjugated systems characterized by delocalized electrons [35].

### 4.3.3 Parameterization

The choice of a proper force field tends to be a delicate topic as most are not “general” force fields and apply only to a very narrow range of systems [110]. For highly specific systems, one is therefore required to develop and parameterize a force field when no applicable sets exist. Parameterization is handled through optimization of the parameters in the analytical function to reproduce observed experimental data (when available), supplementing with high-level electronic structure calculations to increase the sample space [28, 35, 64, 66, 116]. Possible data to utilize are results from scattering experiments, spectroscopic measurements, thermophysical data, elastic constants, phonon spectra, dielectric properties, and NMR studies [66]. Dielectric, elastic, and lattice-dynamic properties are commonly implemented by modifying the force field to handle polarization (e.g., shell model) [28].

Parameterization can be handled by a simple least-squares minimization method to produce the best fit. Weighting schemes can be employed to give importance to specific deviations. A simple example of one is [35]
\[ Z = \left( \sum_i^{Prop} w_i^2 \sum_j^{Osr} \left( X_{i,j}^{Osr} - X_{i,j}^{calc} \right)^2 \right)^{1/2} \] (4.49)

As *ab initio* methods are becoming more accurate, it is customary to rely solely on these results for parameterization. This grants one the freedom to work with data which is tailored to unusual molecules lacking experimental data and, for condensed phases, properly account for boundary interactions with an infinite environment [13]. Utilization of electronic structure data also has the benefit of allowing one to probe geometries further separated from equilibrium, even accommodating transition states in molecular reactions [35]. In addition, force fields can be parameterized such that they match quantum mechanical energy gradients to give more reliable forces during simulation [35].

Understanding some considerations when designing or implementing a force field can help to speed up computation, thus allowing for longer simulations. As already mentioned, radial cut-offs can be employed for non-electrostatic terms to reduce the number of forces to be calculated and the decrease nearest-neighbor searching (optimally reaching a scaling of $\mathcal{O}(N)$ for these interactions) [64]. This should be accounted for within the model to diminish artefacts created by truncation, allowing the potential to smoothly approach zero as the cut-off value is reached. United atoms can be applied in systems where applicable to decrease the number of interactions computed [13]. Finally, the force field should be simple enough to enable fast computation while still being able to capture the basic physics and phenomena involved.
4.4 Pair-Potentials

4.4.1 Lennard-Jones Potential

Perhaps the most well-known and simplest potential for binary interactions is the Lennard-Jones ($LJ^{12,6}$) model. Lennard-Jones proposed a modification of the Mie potential while studying the virial coefficients and experimental temperature variation of the viscosity in gases [66, 129]. Although the attractive term has theoretical justification based on polarization, the inverse power dependence for the repulsive term is typically attributed to being chosen for mathematical convenience [66].

Owing to its simplicity and ease of implementation (requiring only even powers of the distance), this model continues to be used in many force fields for simulations of large systems [35]. The derivation of the $LJ^{12,6}$ assumes only spherically symmetric, non-polar molecules interacting via London dispersion forces and a strong repulsive interaction [111]. Because of this, the model has been used quite successfully for liquid argon and is often used as a generic first approximation to study the qualitative features of a system [113], although it is generally considered too “hard” of a potential for realistic simulations [64].

The functional form of the $LJ^{12,6}$ model is [1]

$$\phi_{LJ}(r_{ij}) = 4\varepsilon \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^{6} \right]$$  (4.50)

where the parameter $\varepsilon$ is the depth of the well at $\partial \phi_{LJ}/\partial r_{ij} = 0$ and the length $\sigma$ can be shown to be $r_{ij}$ for which $\phi_{LJ}(r_{ij}) = 0$. 
4.4.2 Morse Potential

The Morse potential was proposed in 1929 by Philip Morse in order to evaluate the vibrational energy level of diatomic molecules [66]. It consists of three parameters which describe the dissociation energy \( E_0 \), the equilibrium bond distance \( r_{eq} \), and the spring constant \( k_0 \). This exponential equation has been able to describe vibrational levels of diatomics quite satisfactorily, although there is no theoretical justification for the particular form [13].

\[
\phi_{Morse}(r_{ij}) = E_0 \{ \exp (-2k_0(r_{ij} - r_{eq})) - 2\exp (-k_0(r_{ij} - r_{eq})) \} \tag{4.51}
\]

The long-range part of this equation does not converge to zero as quickly as the \( r^{-6} \) functions (Lennard-Jones and Buckingham) and this has led to some restraint from its use in phases that dissociate, though there are in fact other multipole terms which it probably predicts quite well [64]. Crystals are typically connected with the notion of a collection of oscillators vibrating around an equilibrium position, and the Morse potential has been used for the evaluation of kinetic and structural properties of these systems as they typically do not fall outside of the range of its validity [66]. Performance of the Morse potential is generally better than both the Buckingham and \( LJ^{12,6} \) potentials for smaller systems [64].

4.4.3 Buckingham Potential

The final potential to be discussed is the Buckingham, or \( exp-6 \) potential. As already alluded to, it is known that the overlap of electron wavefunctions gives rise to the repulsive force. The electron density falls off exponentially for a hydrogen atom, so it should be a fairly good approximation to estimate the repulsion force in a similar manner [64]. The attractive force still considers an inverse sixth dependence on
distance, allowing for proper inclusion of dispersion forces [66]. This gives rise to the $exp^{-6}$ interatomic potential [129].

\[
\phi_{exp^{-6}}(r_{ij}) = A_{ij} \exp \left\{ -\frac{r_{ij}}{\rho_{ij}} \right\} - C_{ij} \frac{r_{ij}^6}{r_{ij}^6} \tag{4.52}
\]

The initial installment of the Buckingham potential carried a dipole-quadrupole term ($r^{-8}$) as well, but this form is rarely applied [129]. The $exp^{-6}$ potential the most commonly used for ionic systems and seems to correct the deficiencies in both $LJ^{12,6}$ and Morse potentials [28]. One thing to note about this potential is that it has two critical points – one local minimum at the equilibrium distance and a global maximum located on the approach zero separation ($\phi_{exp^{-6}}(r_{ij}) \to -\infty$ as $r_{ij} \to 0$). However, the energy barrier for this transition is usually on the order of 100 kcal/mol, and this is generally not a problem for most applications (excluding fusion) [64].

### 4.4.4 Long Range Electrostatics

Finally, we come to the elusive electrostatic interactions. It could be said that all of chemistry is based upon the electrostatic potential, as these are the forces governing the stability atoms and their respective bonds. The fact that nuclei are able to shield and cancel the electronic charge in most systems allows for much simplification in terms of the interatomic many-body problem. It is for those systems which do not perfectly cancel out that this discussion is required, and these systems offer the most interesting chemistry.

Electrostatics are grouped into a category known collectively as ‘long-range’ forces. These are often defined as those in which the spatial interaction falls no faster than $r^{-d}$, with $d$ being the dimensionality of the system [1]. In addition to monopole-monopole forces, the three other charged interactions included in this group are monopole-dipole (solvation of ions), monopole-quadrupole (structural stability of pro-
teins), and dipole-dipole interactions (polar association). Excluding the monopoles, all of these arise from an asymmetric internal distribution of electrons about the positively charged nuclei, creating negative and positive sections of a molecule [64]. Asymmetric molecules tend to have permanent dipoles, while symmetric molecules with uneven charge distributions will have a zero dipole moment but higher-order multipoles as a result of electron localization [111]. In comparison to other physical intermolecular energies, electrostatic potentials, when present, comprise the dominant forces associated with bonding. This can be seen by example with the salt crystal $Na^+Cl^-$ at equilibrium, where electrostatic forces give rise to a potential energy that is about $200 \, k_B T$ at room temperature and is thus responsible for the crystal’s stability and very high melting point [111].

The electrostatic potential/force is generally represented by a truncated sum of binary multipole interactions between the constituents of an ensemble, and this has the benefit of being particularly simple to evaluate computationally [35]. The Coulomb potential describes the interaction between point charges in vacuo, allowing for a summation over all of the point charges in the system to determine the contribution from monopole-monopole interactions [28, 111].

$$E_{\text{Coulomb}}(r_{ij}) = \frac{1}{2} \left( \frac{1}{4 \pi \varepsilon r_{ij}} \right) \sum_{j>i=1}^{N} \frac{Q_i Q_j}{r_{ij}}$$  \quad (4.53)

Note that implementation into periodic systems allows for relative ease in finding the coordinates since they are separated by multiples of the unit cell dimensions. In the above equation, $Q_k$ represents the charge located on the ion “$k$” and is usually a multiple of the elementary charge $e$. The dielectric constant, $\varepsilon$, is the permittivity of the environment and included to account for charge ‘screening’ by surrounding molecules [64]. The dielectric constant is often assumed to be that of the permittivity of free space, although this is not necessarily consistent with the approximations
introduced when using atomic partial charges [35]. Instead, Cramer [35] suggested that it can take on multiple values and even be viewed as a parameter of the model. Jensen [64] has also acknowledged this consideration, stating that there is little theoretical justification for it taking on any particular value. Dielectric constants commonly have a range of 1 to 4, and are sometimes described as being distance-dependent to increase computation speeds [64].

Ionic crystals, where the two-body approximation has largest validity, have the property of being formed entirely of charge particles held together largely by Coulomb forces [129]. In addition, their periodicity allows one to separate the geometric lattice from the charges and lattice constant in the Coulomb potential. This is due to the fact that the positions for all of the atoms within the unit cell and neighboring images can be described mathematically by an infinite series. Thus, for a stationary infinite crystal with all of the atoms at equilibrium positions, we can write the electrostatic potential as a Madelung sum (named after Erwin Madelung) [69]. A general form of the Madelung sum is given by

\[ \alpha = \sum_{L} \sum_{i,j} N_{ions} \frac{q_i q_j}{|p_{ij} + L|} \]

in which \( a_{lat} \) is the lattice constant, \( L \) is the vector between the origin of the unit cell and the image cell (normalized by the lattice constant so that it is multiples of real numbers), \( p_{ij} \) is the fractional vector between the two ions, \( N_{ions} \) are the number of ions within the primitive cell, and the summation excludes terms for which \( i = j \) and \( L = (0, 0, 0) \) [129].

It should be noted that the determination of Coulomb forces, even when evaluating Madelung constants for stationary crystals, are only conditionally conver-
gent [28]. This is because of the relative strength of the force and its long-range nature, requiring a very large volume of atoms to be included before forces are negligible. This negates the use of the typically employed cut-off values for intermolecular forces as the range of interaction is much larger than half of the unit cell length [1]. Improper truncations can lead to serious side-effects in calculations, producing sharp gradients in the forces to give inaccurate and non-conservative results [64]. Fortunately, methods have been devised to handle these complications and reduce the dependency below $O(N^2)$.

The Ewald summation technique and its variants are all geared toward increasing calculation efficiency with the implementation of Fourier transforms to handle the periodicity of the system. The basic premise is to split the conditionally convergent sum into a self term and two rapidly convergent sums, one in real-space and the other in reciprocal-space [130]. Rather than expressing the charge density as a sum of delta functions, these methods assume that every particle is surrounded by a periodic, smoothly varying, diffuse charge distribution of the opposite sign. This allows the real-space terms to only account for that part of the charge which is not screened and provide rapid convergence [41]. The diffuse charge is then compensated for in the calculation by a Fourier transform over inverse-space. The self-term, which is included for mathematical convenience in the Fourier analysis, is subtracted to regain the Coulomb energy [41]. The Ewald summation scales as $O(N^{3/2})$ and its variants like the particle-mesh Ewald are generally found to be on the order $O(N \log N)$. Another scheme, called the fast multipole method, splits the contributions into near- and far-fields and utilizes an idea similar to renormalization group theory to handle charges in distant images through a hierarchy of cells, providing scaling with $O(N)$ [113]. However, large systems are required before these values are observed and the maximum error is larger than that given by Ewald methods [64].
Determining the correct atomic charges for ionic systems is a very important task and can lead to substantial errors when not handled properly. This can be seen directly from the form of the electrostatic potential, as only the charge and lattice constant give rise to the energy once an ionic crystal's structure is known. For heteroatomic binuclear crystals at a given lattice constant, the energy will change roughly proportional to square of the charges assigned, giving large errors if these are not estimated correctly. The charges can also either be fixed and placed on the nuclei or bonds, or alternatively they may be computed as a function of the polarization or electronegativity of the environment [35]. It is becoming more and more common to assign these parameters on the basis of fitting to the electrostatic potential from electronic structure methods [13, 64]. Various algorithms have been constructed for evaluating charges, leading to four different classes of charge assignment methodologies, although there is no universally agreed upon procedure [35]:

1. **Class I** charges are based upon some intuitive or arbitrary approach and have no inclusion of quantum mechanical calculations. Fitting charges to produce experimental dipole moments is a possibility. Examples of this type are the Partial Equalization of Orbital Electronegativity [43] and the QEq charge equilibration model [114].

2. **Class II** charges partition the molecular wavefunction into atomic contributions from some arbitrary orbital-based scheme. Examples are the Natural Population Analysis [115] and Mulliken Population Analysis [92].

3. **Class III** charges evaluate some physical observable, such as dipole moments or electron density from X-ray crystallography, and perform electronic structure calculations to fit the data accordingly. The Generalized Atomic Polar Tensor [33] and Atoms-In-Molecules [9, 75] are two instances.

4. **Class IV** charges utilize the results from either *Class II* or *Class III* methods and improve upon them in order to reproduce experimentally determined properties.
Although it is typically not included in MD simulations due to the increased complexity and computation time required (about an order of magnitude larger), exclusion of polarizability is probably one of the main limitations of modern force field methods for polar systems [64]. This phenomenon gives rise to all attractive forces between non-polar molecules, is responsible for the Stark effects, and describes the redistribution of electron density within the presence of an electric field [35]. Numerous methods have been proposed to deal with this effect, though again there is no general consensus on which, if any, are best to implement [35].

### 4.5 External Fields

Interactions of the molecules/particles with the environment are handled by the use of external force fields. These are represented by the $\phi_1$ terms in Eqn. (4.35). There can be any combination of specific interactions (including gravitational fields, magnetic fields, electric fields, pressure induced by pistons, etc.). Some specific interactions that benefit from this type of modeling are transport properties (e.g. conduction), containment (e.g. pores), or mechanical forces (e.g. shearing/stress) [128].
Chapter 5

Computational Platforms

5.1 QUANTUM ESPRESSO Suite

Electronic structure calculations are handled by the QUANTUM ESPRESSO (opEn Source Package for Research in Electronic Structure, Simulation, and Optimization) integrated suite of open-source computer codes [46]. The Kohn-Sham equations are solved within a density functional theory formalism using plane-wave basis sets and pseudopotentials to describe the interaction of nuclei and electrons. Source files and binaries can be downloaded from their website (http://www.quantum-espresso.org) under the GNU General Public License along with plug-ins for advanced calculations and some third-party packages.

Once compiled, using optimized mathematical libraries (BLAS, LAPACK, and FFTW) and parallel algorithms for high performance, the user can simulate many periodic and aperiodic networks, being especially suited for infinite crystalline systems. Ultrasoft and norm-conserving pseudopotentials, as well as projector-augmented waves, can be used in conjunction with many popular exchange-correlation functionals (LDA, GGA, GGA+U). Pseudopotentials can either be downloaded from the QUANTUM ESPRESSO website, taken from other libraries with UPF (Unified Pseu-
dopotential Format) potentials, or created using the atomic code from QUANTUM ESPRESSO [46]. With properly chosen pseudopotentials, the relaxed crystal structures produce lattice constants and other physical quantities which are extremely close to experimentally calculated values, signifying the robust capacity of this software.

This software package offers a multitude of calculations and post-processing tools. Kohn-Sham orbitals and energies for isolated or periodic systems, structural optimizations using Hellmann-Feynmann forces, magnetic and spin-polarized ground-states, \textit{ab initio} MD within a variety of ensembles, and transition-path optimization are just some of the procedures which can be selected. Plotting of quantities such as the charge and spin density, STM images, and electron localization functions can be easily carried out and incorporated with other software (e.g., XCRYSDEN) for further processing.

Structural optimization is performed with the PWscf (v 5.1.0) package, standing for Plane-Wave self-consistent field. This package utilizes an iterative approach with diagonalization techniques at each step to reach self-consistency in the framework of the pseudopotential method [46]. One is able to locate the equilibrium structure from ground-state energies by changing the lattice parameters (lattice constant and \( \omega \) for \( MB_6 \) systems) individually. Other procedures available from the PWscf package include the determination of atomic forces and stresses, macroscopic polarization and Berry phases, orbital magnetization, minimum energy paths with the nudged elastic band method, and Born-Oppenheimer or Car-Parrinello MD.

The PHonon package (v 5.1.0) allows one to calculate vibrational properties such as phonon frequencies, phonon densities of states, interatomic force constants, effects of electric fields, and various other properties of the material. Typical use of PHonon requires one to first set up simulations and locate the ground-state elec-
tronic/atomic configurations with PWscf. The data files generated are then used within Density-Functional Perturbation Theory to calculate second- and third-order derivatives of energy with respect to atomic displacements (and electric fields, if applicable) [46].

Post-processing of the output data files gives one the ability to extract relevant details from the self-consistent field calculations and place them in a format suitable for graphical representations. These routines are handled by the PostProc (v 5.0) package from QUANTUM ESPRESSO. Some of the quantities which can be plotted are charge density, local density of states, STM images, electron localization functions, and various potentials. For multi-dimensional plots, these can also be rendered in different planar slices, giving one the freedom to choose specific axes for contour plots or values along a line.

Refer to Appendix A for examples of input files to generate some of these results.

5.2 DL_POLY Code

The general purpose classical MD software DL_POLY (v 4.05.1) [128] is used in this work for simulating time-dependent phenomena and the applications of different environments. It was developed at Daresbury Laboratory by I.T. Todorov and W. Smith and the software and its license can be obtained online through their website (http://www.ccp5.ac.uk/DL_POLY), free of charge for academic institutions. It is well-suited for large systems of up to a million atoms, implementing parallelism through the domain decomposition strategy [127].

Many molecular systems can be simulated with the current version, including mixtures, crystals, ions with both polarizable and point charges, rigid systems, metals, and glasses. In addition to many popular force field schemes such as CHARMM, AMBER, and OPLSAA [127], the user has a variety of potentials to choose from and
the possibility to define their own. External conditions such as magnetic, gravitational, and electric fields can also be simulated. The integration schemes previously discussed, in addition to many others, can be chosen depending on the user’s preferences [127].

The external force field implemented in DL_POLY which is of critical importance to this project is the electric field. The force generated by an external electric field applies to atoms of specific charges \((q_i)\) and is represented by [127]

\[
\mathbf{F}_i = \mathbf{F}_{i,\text{noE}} + q_i \cdot \mathbf{E}
\]  

(5.1)

with units of \(eV/(\text{Å} \cdot e)\) for the enabled field when \(eV\) is selected as the unit of energy. The directionality is given by three Cartesian vectors and designated in the FIELD file, accompanying the CONFIG and CONTROL files for DL_POLY execution.

Appendix B contains examples of input parameters and files for this code.
Chapter 6

DFT Calculations of Lanthanum Hexaboride

6.1 Pseudopotentials

Various pseudopotentials have been experimented with to obtain satisfactory results. It was found that the ultrasoft pseudopotentials with Perdew-Burke-Ernzerhof exchange-correlation GGA functionals suited our purposes best, as they frequently produced lattice constants with the best fit to published experimental data. The two files used for simulations of $LaB_6$ are “B.pbe-n-van_ak.UPF” and “La.pbe-n-bpaw.UPF”, downloaded from http://www.quantum-espresso.org (using molecular weights of 10.811 and 138.90547 AMU’s, respectively). The first letter of the pseudopotential name corresponds to the atom, followed by ‘pbe’ signifying that it is a Perdew-Burke-Ernzerhof exchange-correlation GGA functional. The ‘n’ refers to the use of a nonlinear core-correction term, and the ‘van_ak’ and ‘bpaw’ represent to the Vanderbilt Ultrasoft and Projector Augmented-Wave (original Bloechl recipe) methods to generate the ultrasoft pseudopotentials.

Comparison with experimental results provide a difference of 0.307% for $\alpha$-$La$
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(DHCP at 24°C), 0.012% for β-La (FCC at 325°C), and 1.121% for γ-La (BCC at 887°C) [49]. In contrast, boron has many different complex allotropes and is rarely found in its pure state. Due to this fact, we chose to verify the boron pseudopotential with lanthanum hexaboride calculations since it has been shown that the lanthanum ions can move relatively freely within each cell, suggesting that lattice parameters are strongly dictated by the boron octahedral sub-lattice [89]. Comparison of relaxed lanthanum hexaboride with experimental values showed an extremely good fit, and an optimal crystallographic refinement parameter of \( \omega = 0.2001 \) was found with a lattice constant of \( a = 4.154 \) Å. For the two sources listed in Table 2.2, errors between reported results for the lattice constant are 0.0543% [83] and 0.0688% [30], respectively.

6.2 Computational Details

Plane-wave self-consistent field calculations allow for the determination of mechanical properties for the lanthanum hexaboride system, as energy values are given as a function of lattice parameter. Electronic band structures are calculated after \( \text{PWscf} \) calculations have been performed, simply specifying a ‘bands’ calculation to produce Kohn-Sham states along symmetry lines. Phonon dispersions and densities of states are obtained from interatomic force constants generated by the \( \text{PHonon} \) package.

General input parameters used for QUANTUM ESPRESSO calculations are given below in Table 6.1. See Appendix A.1 for examples of input files used in this work for the \( \text{PWscf} \) code.
Table 6.1: Input parameters for QUANTUM ESPRESSO files.

### 6.3 Mechanical Properties

The Birch-Murnaghan equation of state for isotropic solids [17] is used to fit the calculated energy and lattice parameters,

\[
E_{\text{tot}}(a) = E_0 + \frac{9V_0B_0}{16} \left\{ \left( \frac{a_0}{a} \right)^2 - 1 \right\}^3 B'_0 + \left( \frac{a_0}{a} \right)^2 \left[ 6 - 4 \left( \frac{a_0}{a} \right)^2 \right] \tag{6.1}
\]

where \(a_0\) is the equilibrium lattice constant and \(V_0\) is the equilibrium volume per atom. The bulk modulus at zero pressure \(B_0\) and its pressure derivative \(B'_0\) are given by

\[
B_0 = -V \left( \frac{\partial P}{\partial V} \right)_{P=0} \quad \text{and} \quad B'_0 = \left( \frac{\partial B}{\partial P} \right)_{P=0} \tag{6.2}
\]

Experimental and calculated values are given below in Fig. 6.1. It can be seen that the calculated values agree quite well with those determined experimentally.
Figure 6.1: $LaB_6$ lattice constant optimization (DFT). Birch-Murnaghan equation of state was fit to produce the bulk modulus, $B_o$. $B_o^{(exp)} = 142-248$ GPa

$a_{lat}^{(exp)} = 4.1512 - 4.1561$ Å

$B_o^{(calc)} = 171$ GPa

$a_{lat}^{(calc)} = 4.154$ Å
6.4 Electronic Properties

6.4.1 Energy Bands

Electronic energy bands for lanthanum hexaboride have been produced from PWscf and generated by the PostProc package. These results can be seen below in Fig. 6.2. No band gap is visible, in accordance with a conductor. Input files for the energy band calculation can be found in Appendix A.2.

![LaB₆ electronic energy bands (DFT)](image)

The absence of a band gap is evidence for a metallic conductor. Overlaps are located around the X-symmetry points.

6.4.2 Phonon Dispersions

Complete phonon dispersion curves calculated from the PHonon package using an $8 \times 8 \times 8$ Monkhorst-Pack grid for phonon wave-vectors $\mathbf{q}$ are shown below in Fig. 6.3.
Acoustic and optical modes are in agreement with *ab initio* results from Gürel [51] (DFT with LDA), and experimental acoustic modes from Smith [121] (up to 480 cm\(^{-1}\)) are also found to be agreeable. See Appendix A.3 for a typical input to QUANTUM ESPRESSO for performing these calculations.

![Figure 6.3: LaB\(_6\) phonon dispersions (DFT).](image)

The eight normal modes from group theory analysis can be seen at the Γ point, giving \(\Gamma = A_{1g} \oplus E_g \oplus T_{1g} \oplus T_{2g} \oplus 3T_{1u} \oplus T_{2u}\).

**Phonon Density of States**

The phonon density of states of lanthanum hexaboride is computed using the PostProc scripts and an example input file can be found in Appendix A.3. These results, shown in Fig. 6.4 are also comparable to those determined by Gürel [51], who used a \(64 \times 64 \times 64\) Monkhorst-Pack grid for \(\mathbf{q}\)-vectors.
Figure 6.4: $LaB_6$ phonon density of states (DFT).
6.5 Thermodynamic Properties

6.5.1 The Quasi-Harmonic Approximation

The quasi-harmonic approximation allows one to incorporate anharmonicities of the lattice vibrations by assuming that these interactions are a result of thermal expansion [36]. Temperature effects of the phonon frequencies are then only dependent on the crystal’s volume and structure, and the lattice dynamics are still treated within the harmonic approximation.

6.5.2 Helmholtz Free Energy

The constant volume free energy for phonons can be derived from the partition function, \( Z \), which is just the Bose-Einstein distribution including zero-point motion and the potential energy of the system [36].

\[
\ln Z = -\frac{1}{k_B T} \left( \varphi + \frac{1}{2} \sum_{\mathbf{q},\nu} \epsilon_{\mathbf{q},\nu} \right) - \sum_{\mathbf{q},\nu} \ln \left[ 1 - \exp \left( -\frac{\epsilon_{\mathbf{q},\nu}}{k_B T} \right) \right]
\] (6.3)

The energy, \( \epsilon_{\mathbf{q},\nu} \), and Helmholtz Free energy, \( F \), are given by

\[
\epsilon_{\mathbf{q},\nu} = \hbar \omega(\mathbf{q},\nu) \quad \text{and} \quad F = -k_B T \ln Z
\] (6.4)

This allows us to write the free energy as

\[
F = \varphi + \frac{1}{2} \sum_{\mathbf{q},\nu} \hbar \omega(\mathbf{q},\nu) + k_B T \sum_{\mathbf{q},\nu} \ln \left[ 1 - \exp \left( -\frac{\hbar \omega(\mathbf{q},\nu)}{k_B T} \right) \right]
\] (6.5)

A plot generated from Phonon is shown below in Fig. 6.5.
Figure 6.5: $LaB_6$ Helmholtz free energy (DFT/QHA). Internal energy and vibrational contributions are shown explicitly.
6.5.3 Entropy

The entropy of a system is defined by the negative partial derivative of the Helmholtz free energy with respect to temperature

$$ S = -\left( \frac{\partial F}{\partial T} \right) $$

(6.6)

giving

$$ S = \frac{1}{2T} \sum_{q,\nu} \hbar \omega(q,\nu) \coth \left( \frac{\hbar \omega(q,\nu)}{2k_B T} \right) - k_B \sum_{q,\nu} \ln \left[ 2 \sinh \left( \frac{\hbar \omega(q,\nu)}{2k_B T} \right) \right] $$

(6.7)

Calculated results for entropy performed in this study are given in Fig. 6.6.

Figure 6.6: LaB$_6$ entropy (DFT/QHA).
6.5.4 Heat Capacity

From thermodynamics, the constant volume heat capacity is found by partial differentiation of internal energy with respect to temperature, holding volume constant.

\[ C_V = \left( \frac{\partial E}{\partial T} \right)_V \]  

(6.8)

We can find the internal energy from its relationship with the Helmholtz free energy \( E = F + TS \) to give

\[ E = F + TS = F - T \frac{\partial F}{\partial T} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} \quad \text{and} \quad \beta = \frac{1}{k_B T} \]  

(6.9)

Differentiation yields

\[ C_V = \sum_{\mathbf{q},\nu} k_B \left( \frac{\hbar \omega_{\mathbf{q},\nu}}{k_B T} \right)^2 \frac{\exp(h\omega_{\mathbf{q},\nu}/k_B T)}{\left[ \exp(h\omega_{\mathbf{q},\nu}/k_B T) - 1 \right]^2} \]  

(6.10)

Excellent agreement has been found between the calculated results of the heat capacity and experimental results, as shown in Fig. 6.7.

6.5.5 Mean-Square Displacements

Mean-square displacements (MSD) allow one to quantify the degree to which atoms move about their equilibrium positions by taking an average of the motions of particles. Using the quasi-harmonic approximation, these can be calculated as

\[ \langle u_z^2 \rangle = \sum_{\mathbf{q}} \frac{\hbar}{NM\omega_{\mathbf{q}}} \left[ \frac{1}{\exp(h\omega_{\mathbf{q},\nu}/k_B T) - 1} + \frac{1}{2} \right] \]  

(6.11)

where \( N \) is the number of primitive cells and \( M \) refers to the atomic masses. The first two plots, Fig. 6.8 and Fig. 6.9, show the average displacements over all three
Figure 6.7: $LaB_6$ constant volume heat capacity (DFT/QHA). DFT calculations and experimental measurements from Peysson et. al. [38] (taken from Gürel [51]).
Cartesian vectors in comparison to published experimental results. Good agreement is found between lanthanum MSD and the work of Booth et. al. [19] in Fig. 6.8. In comparison to Novikov, better agreement is again found with Booth et. al. for the boron MSD values.

![Graph showing MSD vs. Temperature for La and B](image)

**Figure 6.8: La MSD within LaB₆ (DFT/QHA).** Comparison of calculated results with experimental values from Novikov [98] (X-ray diffraction) and Booth et al [19] (neutron diffraction).

**QUANTUM ESPRESSO** also allows one to split the average displacements into their constituent Cartesian components. The plots generated for lanthanum and boron can be found in Fig. 6.10 and Fig. 6.11, respectively. MSD values for lanthanum in all three directions show good homology, whereas some anisotropy is found for the boron lattice. Vibrations in the x-direction appear to be about 30% as much as the other two directions for the hexaboride structure.
Figure 6.9: B MSD within LaB$_6$ (DFT/QHA).
Comparison of calculated results with experimental values from Novikov [98] (X-ray diffraction) and Booth et al [19] (neutron diffraction).
Figure 6.10: Cartesian components of La MSD (DFT/QHA). Displacements are approximately equal along all three axes.
Figure 6.11: Cartesian components of $B$ MSD (DFT/QHA). Anharmonicity is observed for the $u_x^2$ component.
Chapter 7

Energy Surfaces and Interatomic Potentials

7.1 Energy Surfaces

The energy surface can be estimated from self-consistent DFT calculations as a function of a characteristic distance such as the lattice constant to give cohesive energy per atom or unit cell. As shown in Section 4.3, the total energy of a molecular or atomic system is given by

$$E_{\text{total}} = \sum_i \phi_1(q_i) + \sum_{i>j} \phi_2(q_i, q_j) + \sum_{i>j} \sum_{k>j>i} \phi_3(q_i, q_j, q_k) + \cdots$$

(7.1)

where $\phi_1(\cdot)$ corresponds to the energy of atom “$i$” in vacuum or at infinite separation (i.e., wall energy), $\phi_2(\cdot)$ corresponds to pair-potential interactions, and $\phi_3(\cdot)$ represents third-body interactions. The summation notation indicates that only distinct pairs or triplets are considered to avoid overcounting of the interatomic interactions.
Alternatively, the energy expression can be written as

$$E_{\text{total}} = \sum_i \phi_1(q_i) + \frac{1}{2!} \sum_i \sum_j \phi_2(q_i, q_j) + \frac{1}{3!} \sum_i \sum_j \sum_k \phi_3(q_i, q_j, q_k) + \ldots \quad (7.2)$$

which corrects for the overcounting of the interactions. If one is interested in isolating the energy contribution for a single atom, this can be done with

$$E_i = \phi_1(q_i) + \frac{1}{2!} \sum_j \phi_2(q_i, q_j) + \frac{1}{3!} \sum_j \sum_k \phi_3(q_i, q_j, q_k) + \ldots \quad (7.3)$$

The pair-potentials $\phi_2(q_i, q_j)$ are very important for MD studies, and are functions of the separation distance between atoms ($r_{ij} = |q_i - q_j|$). For systems with cubic periodic crystal structures, the pair-potential can be written as a function of the lattice constant $a$ as follows:

$$\phi_2(q_i, q_j) = \phi_2\left(|x_{ij}|a\right) \quad (7.4)$$

where $x_{ij}$ is the vector between atoms “$i$” and “$j$”, normalized by the lattice constant $a$. If we assume that atom “$i$” is at the origin of the coordinate system describing the crystal structure, then for any atom “$j$” in a neighboring (image) cell, the vector $r_{ij}$ becomes

$$r_{ij} = |x_{ij}|a = ma_1 + na_2 + la_3 \quad (7.5)$$

where $a_k$ are the lattice vectors for the atomic structure and the indices $m$, $n$, and $l$ exclude the point $(m, n, l) = (0, 0, 0)$ to avoid self-interactions. For lattices which are not simple cubic, an additional vector is included to describe the separation of atoms “$i$” and “$j$” within the unit cell.
7.2 Interatomic Pair-Potentials

Assuming that only pairwise potentials contribute to the total cohesive energy of \( \text{LaB}_6 \), the total energy can be approximated by

\[
E(a) = \phi_{\text{La}} + \sum_i \phi_{\text{La-La}} \left( d_i^{(1)}(a) \right) + \sum_i \phi_{\text{B-B}} \left( d_i^{(2)}(a) \right) + \sum_i \phi_{\text{La-B}} \left( d_i^{(3)}(a) \right) \tag{7.6}
\]

where \( d_i^{(k)}(a) \) are distance functions for atom pair “\( i \)” and structure “\( k \)” for the \( \text{La-La} \), \( \text{B-B} \), and \( \text{La-B} \) substructures, respectively. For example, the energy per atom for the \( \text{La-La} \) structure (simple cubic with lattice constant \( a \)) is given by the expression

\[
E_{\text{La-La}}(a) = \phi_{\text{La}} + \sum_{(m,n,l) \neq (0,0,0)} \phi_{\text{La-La}} \left( \sqrt{m^2 + n^2 + l^2} a \right) \tag{7.7}
\]

where the factor \( 1/2 \) is given to avoid overcounting the interactions.

The other two interactions are more complex. From Table 2.1, notice that there are six distances which must be accounted for within the \( \text{La-B} \) potential. Taking any lanthanum atom as a basis, these six distances between the \( \text{La} \)-ion and each of the borons within a single octahedron must be computed (Fig. 7.1). Incorporating the crystallographic parameter \( \omega \), we can decompose the distances and derive the energy per unit cell for the \( \text{La-B} \) interactions as

\[
E_{\text{La-B}}(a) = 3 \sum_{k=0} \sum_{(m,n,l)} \phi_{\text{La-B}} \left( \sqrt{(m + (-1)^k \omega)^2 + (n + \frac{1}{2})^2 + (l + \frac{1}{2})^2} a \right) \tag{7.8}
\]

The absence of a 1/2 factor in Eqn. (7.8) is due to the fact that we are only considering the interactions from the standpoint of the \( \text{La} \) ion, so no overcounting occurs.

For the \( \text{B-B} \) interactions, any of the boron atoms in the unit cell can be taken as reference. As with the \( \text{La-B} \) case, there are again six interactions which need to be handled, as can be seen from the \( 2 \times 2 \times 2 \) cell in Fig. 7.2. Each boron interacts
Figure 7.1: $LaB_6$ unit cell.
Lanthanum atoms on the corners of the cubic cell (yellow) and boron atoms in octahedral structure at the center (fuschia).
with all of the other borons within the unit cell, in addition to all of the images in
neighboring image cells up to a given cut-off. Including all of the $B-B$ interactions,
the energy per boron atom within a unit cell can be written as

$$
E^{B-B}(a) = \phi_B^2 + \frac{1}{2} \sum_{(m,n,l) \neq (0,0,0)} \phi_{B-B} \left( \sqrt{m^2 + n^2 + l^2 a} \right) + \frac{1}{2} \sum_{(m,n,l)} \phi_{B-B} \left( \sqrt{m^2 + n^2 + (l - 2\omega)^2 a} \right)
+ \sum_{k=0} \sum_{(m,n,l)} \phi_{B-B} \left( \sqrt{m + (-1)^k \left( \frac{1}{2} - \omega \right)} \right)^2 + n^2 + l^2 a \right)
$$

(7.9)

Figure 7.2: LaB$_6$ crystal structure for several unit cells. Lanthanum atom on the corners of the cubic cell (yellow) and boron atoms in octahedral structure at the center (fuschia).
7.2.1 Möbius Inversion Method

Having the lattice energy as a function of pair-potential allows one to connect the QUANTUM ESPRESSO data generated to a system of pairwise interactions for each lattice type. The next step is to determine a suitable form of the potential such that is able to incorporate the many-body effects and sufficiently reflect the energy of the system as the atomic locations fluctuate and are no longer fixed. The Möbius inversion of an energy surface (per atom in crystal structures) is an attractive way to extract these binary potentials, assuming that they are accurate enough to describe the properties of interest and convergent formulae can be obtained. In solids it is not uncommon that third-body contributions to the potential energy are important and should be taken into consideration depending on the accuracy required and purpose of the calculations. However, we make the assumption that the total energy can be decomposed into pairwise interactions in order to produce potentials which can both faithfully reproduce the fully quantum mechanical energy calculated for the system and further be implemented into a MD simulation.

Inversion of total energies to extract pair-potentials has seen many successful attempts in recent literature for systems involving ionic crystals [137, 138, 139, 140, 141, 142], metals [29, 32, 87, 95, 112, 134], semiconductors [25, 136], nitrides [143], and migration of gases within metal frameworks [37]. A short introduction to the formalism will be given here — for further information the reader is directed to any of the papers listed above or the book by Nan-Xian Chen [31].

The Möbius inversion method utilizes classical Gaussian elimination to produce pairwise interactions from the total cohesive energy generated from \textit{ab initio} methods. For example, in a 1-D lattice, the total energy of a particular lattice point is a
sum of pair-potentials of the form

\[ \mathbb{E}(x) = \sum_{n=1}^{\infty} \phi(nx) \]  

(7.10)

such that subtracting successive energies at increasing distances (i.e., Gaussian elimination) from the total energy will generate the pair-potential from \( \mathbb{E}(x) \):

\[ \phi(x) = \mathbb{E}(x) - \mathbb{E}(2x) - \mathbb{E}(3x) - \mathbb{E}(5x) + \mathbb{E}(6x) + \cdots = \sum_{n=1}^{\infty} \mu(n) \mathbb{E}(nx) \]  

(7.11)

where the Möbius inversion function is given by

\[ \mu(n) = \begin{cases} 
1 & \text{if } n = 1, \\
(-1)^s & \text{if } n = \prod_k p_k (p_i \neq p_j \text{ if } i \neq j), \\
0 & \text{otherwise}.
\]  

(7.12)

In the above formula for \( \mu(n) \), \( p_i \) refers to a prime number, such that \( n \) should be a product of \( k \) distinct prime numbers if a value other than zero is to be obtained.

For a three-dimensional system, the inversion is more complex and requires knowledge of the interatomic spacing between atoms within the lattice and the multiplicity at specific distances. In a manner similar to the CGE method (Carlsson-Gelatt-Ehrenreich [26]), Nan-Xian Chen has developed a convergent method to produce pairwise interaction potentials utilizing the Möbius inversion scheme. The total energy of a lattice site is again assumed to be a sum of pair-potentials, utilizing the distance function (from above) and the multiplicity at a specific distance [31]

\[ \mathbb{E}(x) = \frac{1}{2} \sum_{n=1}^{\infty} r(n) \phi(b(n) x) \]  

(7.13)

where \( x \) is the nearest-neighbor distance between the interacting atoms within the
lattice, \( r(n) \) is the \( n^{th} \)-coordinatation number, and \( b(n) \) is the \( n^{th} \)-neighbor distance. In order for the inversion to converge properly, the components of \( b(n) \) need to form a multiplicative semigroup such that \( b(x)b(y) = b(xy) \). This helps to reduce the amount of noise generated during the inversion process. In reality, most three-dimensional structures commonly found do not have a set of distances forming a multiplicative semigroup. Instead, they are approximated with an unclosed set \( \{ b_0(n) \} \) with \( b_0(n) = \sqrt{n} \), (as distances are defined by the square root of a sum of squares). This introduces some artefacts in the calculation, producing one “ghost” location in every 8 or 16 values of \( n \) for a simple cubic or face-centered cubic structure, respectively. This artefact comes from the fact that, although \( \sqrt{7} \) is completely valid value of \( b(n) \) for the inversion (e.g. \( \sqrt{1}\sqrt{7} = \sqrt{7} \)), there is no way to generate this distance from a sum of three squares of natural numbers. The same applies to a face-centered cubic lattice with \( b(n) = \sqrt{15} \). These distances are part of the natural set of the multiplicative semi-group formed but no atoms exist at these loci. The body-centered cubic lattice is also possible to invert, though a large proportion of the points utilized end up being these ghost points, so accuracy and convergence of the inversion are sometimes questionable. A modified multiplicity function \( r_0(n) \) is therefore used to correct for locations generated without actual atoms.

To invert the energy according to the Chen-Möbius method [31], the modified Möbius function \( J(n) \) (similar in effect to the Möbius inversion function) of the multiplicity function \( r(n) \) is employed:

\[
E(x) = \frac{1}{2} \sum_{n=1}^{\infty} r(n)\phi(b(n) x) \implies \phi(x) = 2 \sum_{n=1}^{\infty} J(n)E(b(n) x)
\] (7.14)
in which the values of multiplicity are modified to give

\[
    r(n) = \begin{cases} 
    r_0(b_0^{-1}(b(n)) & \text{if } b(n) \in b_0(n), \\
    0 & \text{if } b(n) \notin b_0(n). 
    \end{cases}
\] (7.15)

where \( b_0(n) \) and \( r_0(n) \) are the actual distances and degeneracies of the lattice in question. The Dirichlet inverse, \( J(n) \), is given by

\[
    \sum_{b(m)b(n)=b(k)} J(n) r(m) = \delta_{k,1}
\] (7.16)

and can be found by simple iterative techniques. In Eqn. (7.16) above, the summation is over all factors \( b(m) \) and \( b(n) \) of \( b(k) \) within the semi-group which satisfy the relation \( b(m)b(n) = b(k) \).

As one may have guessed, the \( LaB_6 \) structure is extremely complex compared to other primitive lattices. Although the inversion is possible for the \( B-B \) and \( La-B \) interactions within \( LaB_6 \), they introduce a plethora of ghost points, so alternative methods are employed to generate the pair-potentials for each of the sub-lattices. However, the energy summations given in Section 7.2 will still be of use to check that the pair-potentials generated are able to accurately reproduce the correct energy for the system.

### 7.2.2 Model Systems

Various simple lattices are inverted for pure lanthanum, pure boron, and lanthanum-boron systems to produce pairwise potentials for these interactions. Starting with the total energy generated from a PWscf calculation in QUANTUM ESPRESSO, we
can write the total energy for a system of atoms in substructure “k” as

\[ E(a) = \phi^0 + \frac{1}{2} \sum_i \phi_{\text{pair}} \left( d_{ij}^{(k)}(a) \right) \]  

(7.17)

The energy at infinite separation, \( \phi^0 \), can be approximated by expanding the lattice such that the energy no longer appreciably changes with respect to lattice constant. This can be observed below in Fig. 7.3, where the energy converges at a value of \( a \) near 10.5 Å.

Figure 7.3: DFT calculated energy for a lanthanum face-centered cubic lattice. The isolated atom energy \( \phi^0 \) is approximated at the final lattice constant value.

The three geometries [31] utilized for inversion of homatomic interactions are the simple cubic, face-centered cubic, and body-centered cubic lattices. Energy per
atom as a function of some distance “x” for each of these can be written as

\[ E^{SC}(x) = \phi^o + \frac{1}{2} \sum_{(m,n,l) \neq (0,0,0)} \phi_{pair} \left( \sqrt{m^2 + n^2 + l^2} \cdot x \right) \]  
(7.18)

\[ E^{FCC}(x) = \phi^o + \frac{1}{2} \sum_{(m,n,l) \neq (0,0,0)} \phi_{pair} \left( \sqrt{m^2 + n^2 + l^2} \cdot \sqrt{2} \cdot x \right) 
+ \frac{3}{2} \sum_{(m,n,l)} \phi_{pair} \left( \sqrt{\left(m - \frac{1}{2}\right)^2 + \left(n - \frac{1}{2}\right)^2 + l^2} \cdot \sqrt{2} \cdot x \right) \]  
(7.19)

\[ E^{BCC}(x) = \phi^o + \frac{1}{2} \sum_{(m,n,l) \neq (0,0,0)} \phi_{pair} \left( \frac{\sqrt{m^2 + n^2 + l^2}}{\sqrt{3}} \cdot \sqrt{4} \cdot x \right) 
+ \frac{1}{2} \sum_{(m,n,l)} \phi_{pair} \left( \sqrt{\left(m - \frac{1}{2}\right)^2 + \left(n - \frac{1}{2}\right)^2 + \left(l - \frac{1}{2}\right)^2} \cdot \sqrt{\frac{4}{3}} \cdot x \right) \]  
(7.20)

Since each of these structures has a different number of atoms within the unit cell, the total energy must be divided so that it reflects this relationship. For the heteroatomic La–B interaction, the L1_2 structure is easily invertible and allows one to produce an interaction between a cation and three anions. Once the respective homatomic interactions and isolated atomic \( \phi^o \) energies have been removed, the heteroatomic energy per atom for the L1_2 structure with the cation as reference is

\[ E^{L1_2}(x) = 3 \sum_{(m,n,l)} \phi_{pair} \left( \sqrt{\left(m - \frac{1}{2}\right)^2 + \left(n - \frac{1}{2}\right)^2 + l^2} \cdot \sqrt{2} \cdot x \right) \]  
(7.21)

### 7.2.3 Approaches to Potential Development

After the pairwise interactions have been extracted from the inversion, the potential obtained is essentially exact for a static system. The next step is to fit the data to a form more suitable for MD simulations. The Morse potential was chosen for
fitting purposes to homatomic interactions, and heteroatomic interactions were represented by either a Morse or Buckingham potential. Different methodologies were employed to develop two sets of potentials to describe the lanthanum hexaboride system. For the first set, the potentials were chosen to mimic equilibrium data as best as possible, employing MD simulations as a final step to generate parameters which accurately reproduce MSD data. The second set was developed to produce a system which resembles the dynamic behavior, utilizing a combination of MD and DFT data to give the potentials the correct dynamics.

As each of the “general” interatomic potentials are only able to describe a specific family of curves, matching the inversion exactly is not always an option, and sacrifices must be made in precision. For the dynamics to be accurately modeled, the potentials should follow the inversion as closely as possible in the regions where important interactions are likely to occur. In a molecular crystal, atomic positions are typically constrained to a small subset of values compared to gases or liquids, so the range of interactions required for keeping stability is limited. To give the right energetics around the equilibrium distance, the potentials were parameterized such that $r_{eq}$ and $E_0$ are identical to those obtained by the inversion. For repulsive interactions, any form which keeps the atoms from overlapping electronic shells is generally sufficient for dynamics, so the sacrifice is made in this range. The region extending beyond the equilibrium separation is very important for keeping atoms bonded, driving them towards a more energetically favorable state or complete isolation depending on distances involved. The potential is therefore shaped so that distances at and beyond $r_{eq}$ give the best fit. This parameterization scheme will be referred to as “Method I” ($MI$).

As already mentioned, the potentials used for fitting purposes are unlikely to capture the inversion properly. Since static properties are reflected in equilibrium
data, lattice energies can give insight into whether or not the pair-potentials are able to reproduce the correct geometry of a system. Even small deviations in pairwise interactions can lead to substantial inconsistencies in the energetics for a system of atoms, leading to erroneous results when placed in a MD framework. For this reason, an alternative method is designed to fit the model potential to the static lattice energies calculated from DFT.

To produce the “best” fit to the lattice energies, parameters generated from MI are taken as an initial basis for further optimization. The same radial cutoffs employed in DL_POLY (12 Å) are used as a constraint with pairwise interaction energy summations over the lattice, generating the lattice energy per cell (or atom, depending on the basis used) for a specific lattice. A preferential weighting function, shown below in Fig. 7.4 for the lanthanum face-centered cubic lattice, is used to give a greater relevance to data at the equilibrium distance and on the upward slope to larger lattice constants. In this way, the transient behavior is still a major factor in the development of the potential. Sum-of-squares energy differences with the weighting function were calculated with

$$\text{Error} = \sum_{i=0}^{N} W(a_i) \left( \varepsilon_{DFT}(a_i) - \varepsilon_{calc}(a_i) \right)^2$$  \hspace{1cm} (7.22)

where the set \(\{a\}\) is over the values of lattice constants used with QUANTUM ESPRESSO.

To begin the optimization procedure, a set of 1200 new parameter sets are generated by randomly changing any (or all) of the initial parameter values (\(r_{eq}\), \(E_0\), and \(k_0\)) by \(\pm 140\%\) and recalculating the lattice energy. The top 15 of these sets with the lowest sum-of-squares error are then selected for a second round of “annealing”. Using a method similar to the Metropolis Monte Carlo algorithm, the values are again randomly chosen to change by \(\pm 50\%\), moving to the next value only if it reduces the error. After 200 iterations, the parameters are then slowly relaxed to their final val-
ues. In this process, each of the three parameters change by ± 0.05% per iteration, creating six new values to test. A step is taken in the direction that gives the lowest error, and this is continued until a local minimum has been found. This method will be referred to as “Method II” (*MII*).

After the potentials have been developed with static DFT data, MD simulations are utilized on selected interactions to improve the dynamics of the system. These will be discussed in subsequent sections when implemented.

![Weighting function for a lanthanum face-centered cubic lattice.](image)

*Figure 7.4: Weighting function for a lanthanum face-centered cubic lattice.*

*Left Axis:* Value of the weighting function. *Right Axis:* Lanthanum face-centered cubic lattice energy. Preferential treatment is given to the equilibrium lattice constant and larger values approaching infinite separation.
7.3 Pseudopotential Validation

Two types of pseudopotentials are chosen to compare their effect on lattice energies and inversions. Both norm-conserving and ultrasoft pseudopotentials have their merits for different types of systems, so it is instructive to see whether one was better suited for lanthanum hexaboride. Since boron has a more complex set of bonding structures, lattice energies and inversions for boron in a variety of theoretical lattices are computed. Lattice energies generated from QUANTUM ESPRESSO are shown for simple cubic, face-centered cubic, and body-centered cubic boron crystals in Fig. 7.5, Fig. 7.6, and Fig. 7.7, respectively. Note that the difference in lattice energies between different lattice-types is largely dependent on the number of atoms within a unit cell.

![Graph showing cohesive energy for simple cubic boron.](image)

**Figure 7.5**: Cohesive energy for simple cubic boron. Comparison of norm-conserving and ultrasoft pseudopotentials. Each unit cell has one atom.
Figure 7.6: Cohesive energy for face-centered cubic boron. Comparison of norm-conserving and ultrasoft pseudopotentials. Each unit cell has four atoms.

As one can see, the differences in lattice energies between the two pseudopotentials is negligible. In some cases they overlap almost exactly. However, the ultrasoft pseudopotential was chosen for this work as it allows for better computational convergence at higher lattice constants.

Owing to the high degree of similarity in the lattice energies, inversions obtained from both pseudopotentials for each lattice are also extremely close. To give a comparison of the inverted pair-potentials, Fig. 7.8 shows the squared deviations for the two pseudopotentials. As one can see, differences are largest in the repulsive region, moving closer to the ionic radius of boron ($r_{\text{ion}} = 0.25 \text{ Å}$ [88]). In fact, this is where the distinction between the two pseudopotentials is most relevant, as the cut-off radii, and therefore orbital shapes, are different. This leads to dissimilar in-
Figure 7.7: Cohesive energy for body-centered cubic boron. Comparison of norm-conserving and ultrasoft pseudopotentials. Each unit cell has two atoms.
interactions between the atoms at close distances as electron density distributions are heavily dependent on orbital geometries and their overlap. It is possible that some of the errors are numerical, although inversions were fit with a cubic spline directly from DFT data and analyzed within the same loop. For reference, typical lengths for boron interactions within the hexaboride structure are between 1.66 Å and 1.76 Å, producing a discrepancy in the pairwise potentials of at most 0.1 eV between the two pseudopotentials in the highly repulsive region.

![Graph](image)

Figure 7.8: Sum-of-squares error between pseudopotential inversions. Values are calculated as \((\phi_{NC}(r) - \phi_{US}(r))^2\). Regions where the dip falls below the graph have errors of zero. All values converge to zero after \(r = 9\,\text{Å}\).

\(NC = \text{Norm-Conserving, US = Ultrasoft}\).

Having chosen the ultrasoft pseudopotentials for this work, an additional validation step for lanthanum was performed. Lattice constants for three bulk phases of lanthanum have been computed with DFT using the ultrasoft pseudopotential.
Table 7.1 shows the calculated and experimentally determined lattice constants for the $\alpha$-, $\beta$-, and $\gamma$-phases of lanthanum.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Crystal Structure</th>
<th>DFT (Å)</th>
<th>Experiment (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>DHCP (298 K)</td>
<td>$a = 3.805$</td>
<td>$a = 3.774$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$c = 12.271$</td>
<td>$c = 12.171$</td>
</tr>
<tr>
<td>$\beta$</td>
<td>FCC (698 K)</td>
<td>$a = 5.302$</td>
<td>$a = 5.303$</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>BCC (1160 K)</td>
<td>$a = 4.212$</td>
<td>$a = 4.26$</td>
</tr>
</tbody>
</table>

Table 7.1: Lattice constants for bulk lanthanum.
Ultrasoft pseudopotentials are used to locate the equilibrium lattice constants within QUANTUM ESPRESSO. Reference: [49].
7.4 Lanthanum Homatomic Potential

The $La-La$ interaction is fit to a Morse potential with the two schemes highlighted above ($MI$ and $MII$) for simple cubic, face-centered cubic, and body-centered cubic lattice. In contrast to boron, this binary interaction has the advantage of being experimentally realizable, forming stable structures in both face-centered and body-centered cubic lattices. Very good agreement is observed with DFT-calculated and experimental lattice constants for lanthanum, being at most in error by 1.121% for the high-temperature phase.

Another point to make is that the pairwise interaction potential is well-suited for describing lanthanum. Transition metals with low oxidation states typically have very little orbital mixing and no electronic asymmetries [24]. Lanthanum is generally in the $+2$ or $+3$ oxidation states, losing one electron in the $5d$-orbital and two electrons in the $6s$-orbital. This creates a spherically symmetric distribution of outer electron shells, precisely the interaction that pairwise potentials describe best.

7.4.1 Simple Cubic Lanthanum

Although lanthanum does not form a stable simple cubic phase, it is found in this geometry within the hexaboride lattice. Therefore, getting an accurate potential for the simple cubic atomic distance-relationship will give insight into whether the pair-potentials derived from observed phases ($FCC$ and $BCC$) are readily transferable into alternative structures. The pair-potentials and lattice energies for simple cubic lanthanum are depicted in Fig. 7.9 and Fig. 7.10 below. Note the effect of utilizing only a single family of curves, as the $MI$ potential produces a less stable and larger lattice. The $MII$ potential recreates the lattice energy well but strongly deviates from the Möbius inversion pair-potential ($E_0$ is 36.7% lower).

A summary of relevant data for simple cubic lanthanum potentials and lattice
Figure 7.9: Simple cubic lanthanum pair-potentials.
Figure 7.10: Simple cubic lanthanum cohesive energy per unit cell.
energies is shown in Table 7.2 and Table 7.3, respectively.

<table>
<thead>
<tr>
<th>Curve</th>
<th>$r_{eq}$ (Å)</th>
<th>$E_0$ (eV)</th>
<th>$k_0$ (Å$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Morse Method I</td>
<td>4.2328</td>
<td>0.58706</td>
<td>1.2162</td>
</tr>
<tr>
<td>Morse Method II</td>
<td>4.2303</td>
<td>0.37130</td>
<td>0.8634</td>
</tr>
</tbody>
</table>

Table 7.2: Morse parameters for simple cubic lanthanum potentials.

<table>
<thead>
<tr>
<th>Curve</th>
<th>$a_{eq}$ (Å)</th>
<th>$E_{min}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Morse Method I</td>
<td>3.9576</td>
<td>-2.9992</td>
</tr>
<tr>
<td>Morse Method II</td>
<td>3.3742</td>
<td>-3.5434</td>
</tr>
<tr>
<td>Möbius Inversion</td>
<td>3.4158</td>
<td>-3.4974</td>
</tr>
<tr>
<td>QUANTUM ESPRESSO</td>
<td>3.4132</td>
<td>-3.4975</td>
</tr>
</tbody>
</table>

Table 7.3: Unit cell cohesive energy for simple cubic lanthanum.
7.4.2 Face-Centered Cubic Lanthanum

Lanthanum transitions from a double-hexagonal close-packed structure to a face-centered cubic structure at a temperature of 310°C. It then stays in this configuration until a temperature of 865°C is reached, just 53°C below its melting temperature [49]. This suggests it is a highly stable system, and since the face-centered cubic inversion has the least amount of “ghost” points, the potential obtained should satisfactorily describe the interactions. Plots of pair-potential energies (Fig. 7.11) and lattice energies (Fig. 7.12) show these relationships. Again, MI produces a larger lattice constant and MII has a much lower pairwise energy minimum.

Data for the face-centered cubic lanthanum potentials is shown in Table 7.4 and Table 7.5.
Figure 7.12: Face-centered cubic lanthanum cohesive energy per unit cell.

<table>
<thead>
<tr>
<th>Curve</th>
<th>$r_{eq}$ (Å)</th>
<th>$E_0$ (eV)</th>
<th>$k_0$ (Å$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Morse Method I</td>
<td>4.2114</td>
<td>0.54262</td>
<td>1.1728</td>
</tr>
<tr>
<td>Morse Method II</td>
<td>4.3341</td>
<td>0.34210</td>
<td>0.8276</td>
</tr>
</tbody>
</table>

Table 7.4: Morse parameters for face-centered cubic lanthanum potentials.

<table>
<thead>
<tr>
<th>Curve</th>
<th>$a_{eq}$ (Å)</th>
<th>$E_{min}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Morse Method I</td>
<td>5.6953</td>
<td>-16.915</td>
</tr>
<tr>
<td>Morse Method II</td>
<td>5.1828</td>
<td>-16.548</td>
</tr>
<tr>
<td>Möbius Inversion</td>
<td>5.3012</td>
<td>-16.378</td>
</tr>
<tr>
<td>QUANTUM ESPRESSO</td>
<td>5.3020</td>
<td>-16.378</td>
</tr>
</tbody>
</table>

Table 7.5: Unit cell cohesive energy for face-centered cubic lanthanum.
7.4.3 Body-Centered Cubic Lanthanum

The body-centered cubic phase of lanthanum is the last structure reached before melting occurs. It is not anticipated that the pair-potential will reflect a stable system, as the actual interactions must lead to some mobility due to its high temperature and proximity to a phase change. This is reflected by its reduction in dissociation energy, $E_0$, in comparison with the other two phases. Calculated energies for the interatomic interactions and lattice energies are illustrated in Fig. 7.13 and Fig. 7.14, respectively.

Figure 7.13: Body-centered cubic lanthanum pair-potentials.

Morse parameters and lattice energy extreme points for body-centered cubic lanthanum are given in Table 7.6 and Table 7.7, respectively.
Figure 7.14: Body-centered cubic lanthanum cohesive energy per unit cell.

Table 7.6: Morse parameters for body-centered cubic lanthanum potentials.

<table>
<thead>
<tr>
<th>Curve</th>
<th>(r_{eq} (\text{Å}))</th>
<th>(E_0 (eV))</th>
<th>(k_0 (\text{Å}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Morse Method I</td>
<td>4.1860</td>
<td>0.51841</td>
<td>1.1379</td>
</tr>
<tr>
<td>Morse Method II</td>
<td>4.3087</td>
<td>0.34166</td>
<td>0.8412</td>
</tr>
</tbody>
</table>

Table 7.7: Unit cell cohesive energy for body-centered cubic lanthanum.

<table>
<thead>
<tr>
<th>Curve</th>
<th>(a_{eq} (\text{Å}))</th>
<th>(E_{min} (eV))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Morse Method I</td>
<td>4.4808</td>
<td>-8.1956</td>
</tr>
<tr>
<td>Morse Method II</td>
<td>4.1157</td>
<td>-8.0152</td>
</tr>
<tr>
<td>Möbius Inversion</td>
<td>4.2070</td>
<td>-7.8982</td>
</tr>
<tr>
<td>QUANTUM ESPRESSO</td>
<td>4.2123</td>
<td>-7.8983</td>
</tr>
</tbody>
</table>
7.4.4 Comparison of Lanthanum Potentials

Six different interatomic potentials have been created to describe La–La interactions. These are grouped into two sets for comparison, the first being from MI (Fig. 7.15) and the second from MII fits (Fig. 7.16). The relaxed MII potentials seem to show better reproducibility, although the pair-potentials do not compare well with the inversion. Averaged Morse parameters for MI are $r_{eq} = 4.2101 \pm 0.0234$, $E_0 = 0.54938 \pm 0.03484$, and $k_0 = 1.1756 \pm 0.0392$. The MII potentials give $r_{eq} = 4.2910 \pm 0.0541$, $E_0 = 0.35169 \pm 0.01699$, and $k_0 = 0.8441 \pm 0.0181$.

![Figure 7.15: Morse Method I lanthanum pair-potentials. The $r_{eq}$ and $E_0$ are fixed to values obtained from lattice inversion.](image-url)
Figure 7.16: Morse Method II lanthanum pair-potentials. Parameters are relaxed to fit lattice energy.
7.5 Boron Homatomic Potential

Pure boron is most thermodynamically stable in the β-rhombohedral phase [39]. The unit cell is an extremely intricate structure, containing more than 300 atoms per unit cell bonded within a system of fused icosahedra [99]. To circumvent the potential problem of inverting such a complex structure, the lattice energies for boron in theoretical simple cubic, face-centered cubic, and body-centered cubic phases are computed.

7.5.1 Simple Cubic Boron

Fitted pair-potentials and inversions of simple cubic boron are compared for pairwise interactions and lattice energies, shown in Fig. 7.17 and Fig. 7.18, respectively. Strangely enough, the \( MII \) potential has a larger dissociation constant than the inversion, in contrast with lanthanum \( MII \) potentials. In addition, the repulsion for \( MI \) is much softer than either the inversion or MII. The capability of the Morse potentials to capture static lattice energy minima is illustrated in Fig. 7.18. The significance of using \( MII \) is highlighted in this figure, as the \( MI \) repulsion is insufficient and allows for the lattice energy to diverge with \( a \to 0 \). A summary of relevant data for the simple cubic boron system is shown in Table 7.8 and Table 7.9.

<table>
<thead>
<tr>
<th>Curve</th>
<th>( r_{eq} (\text{Å}) )</th>
<th>( E_0 (eV) )</th>
<th>( k_0 (\text{Å}^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Morse Method I</td>
<td>2.6105</td>
<td>0.33276</td>
<td>0.9775</td>
</tr>
<tr>
<td>Morse Method II</td>
<td>2.7184</td>
<td>0.38564</td>
<td>1.1968</td>
</tr>
</tbody>
</table>

Table 7.8: Morse parameters for simple cubic boron potentials.
Figure 7.17: Simple cubic boron pair-potentials.

<table>
<thead>
<tr>
<th>Curve</th>
<th>$a_{eq}$ (Å)</th>
<th>$E_{min}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Morse Method I</td>
<td>0.0000</td>
<td>$-\infty$</td>
</tr>
<tr>
<td>Morse Method II</td>
<td>1.8680</td>
<td>-5.3568</td>
</tr>
<tr>
<td>Möbius Inversion</td>
<td>1.8680</td>
<td>-5.4033</td>
</tr>
<tr>
<td>QUANTUM ESPRESSO</td>
<td>1.8839</td>
<td>-5.4065</td>
</tr>
</tbody>
</table>

Table 7.9: Unit cell cohesive energy for simple cubic boron.
Figure 7.18: Simple cubic boron cohesive energy per unit cell.
The lattice energy for Morse Method I approaches $-\infty$ for small lattice constants, similar to the Coulomb potential.
7.5.2 Face-Centered Cubic Boron

Interactions for face-centered cubic boron can be seen in Fig. 7.19 and Fig. 7.20. The calculated parameters for $MI$ and $MII$ are similar, suggesting that the shape of the inversion is congruent with the Morse potential. However, even the slightest deviation in parameter values between the two potentials can have a significant effect on the recalculated lattice energy, as face-centered cubic lattices with a lattice constant to radial cutoff ratio of 1 : 4 require sums of over 1000 pairwise interactions to compute the unit cell lattice energy. The subtle difference is shown in Fig. 7.20, where the equilibrium lattice constant and energy are drastically shifted for the $MI$ potential.

Figure 7.19: Face-centered cubic boron pair-potentials.

Lattice and pair-potential data for face-centered cubic boron is shown in Table 7.10 and Table 7.11.
Table 7.10: Morse parameters for face-centered cubic boron potentials.

<table>
<thead>
<tr>
<th>Curve</th>
<th>( r_{eq} ) (Å)</th>
<th>( E_0 ) (eV)</th>
<th>( k_0 ) (Å(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Morse Method I</td>
<td>2.6873</td>
<td>0.31660</td>
<td>1.1145</td>
</tr>
<tr>
<td>Morse Method II</td>
<td>2.6488</td>
<td>0.32738</td>
<td>1.2366</td>
</tr>
</tbody>
</table>

Table 7.11: Unit cell cohesive energy for face-centered cubic boron.

<table>
<thead>
<tr>
<th>Curve</th>
<th>( a_{eq} ) (Å)</th>
<th>( \varepsilon_{min} ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Morse Method I</td>
<td>2.3771</td>
<td>-29.157</td>
</tr>
<tr>
<td>Morse Method II</td>
<td>2.8845</td>
<td>-20.270</td>
</tr>
<tr>
<td>Möbius Inversion</td>
<td>2.8483</td>
<td>-20.405</td>
</tr>
<tr>
<td>QUANTUM ESPRESSO</td>
<td>2.8628</td>
<td>-20.411</td>
</tr>
</tbody>
</table>
### 7.5.3 Body-Centered Cubic Boron

Body-centered cubic boron potentials are shown in Fig. 7.21 and Fig. 7.22. The three pair-potentials are all fairly similar. Once again, the boron MI produces a lower lattice constant and stronger cohesive energy.

![Figure 7.21: Body-centered cubic boron pair-potentials.](image)

A summary of relevant data for the body-centered cubic boron potentials is shown in Table 7.12 and Table 7.13.

<table>
<thead>
<tr>
<th>Curve</th>
<th>$r_{eq}$ (Å)</th>
<th>$E_0$ (eV)</th>
<th>$k_0$ (Å$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Morse Method I</td>
<td>2.8444</td>
<td>0.26889</td>
<td>1.0806</td>
</tr>
<tr>
<td>Morse Method II</td>
<td>2.8658</td>
<td>0.27404</td>
<td>1.1075</td>
</tr>
</tbody>
</table>

Table 7.12: Morse parameters for body-centered cubic boron potentials.
Figure 7.22: Body-centered cubic boron cohesive energy per unit cell.

Table 7.13: Unit cell cohesive energy for body-centered cubic boron.
7.5.4 Comparison of Simple Boron Potentials

The three structures described above again give rise to six different interatomic potentials to describe the interactions. These are grouped into two sets for comparison. The first set comprises $MI$ potentials in Fig. 7.23 and all have a similar shape. $MII$ potentials are plotted in Fig. 7.24. Averaged values for $MI$ parameters are $r_{eq} = 2.7141 \pm 0.1192$, $E_0 = 0.30608 \pm 0.03321$, and $k_0 = 1.0575 \pm 0.0714$. $MII$ parameters are $r_{eq} = 2.7443 \pm 0.1108$, $E_0 = 0.32902 \pm 0.05582$, and $k_0 = 1.1803 \pm 0.0661$.

It should be noted that the dissociation energies obtained by all the aforementioned lattices are much smaller than what should be expected for the strong boron bonding. $B$–$B$ bonds are amongst the strongest $2c - 2e^-$ bonds known, having larger dissociation energies than carbon-carbon bonds [47]. Table 7.14 lists some data found for the $B$–$B$ bond strengths. Assuming these reflect the general trend for bonding within boron networks, the calculated $E_0$ energies from theoretical lattices are about 10% of the correct values. This may be a reflection of an incorrect method to determine these binding strengths or perhaps a different pseudopotential is required to accurately capture these energies. Alternative methods are described below to handle this discrepancy.

<table>
<thead>
<tr>
<th>Property</th>
<th>Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boron $\Delta H_{vap}$</td>
<td>4.975$^a$</td>
</tr>
<tr>
<td>Boron $\beta$-Rhombohedral Migration $E_a$</td>
<td>4.75$^b$</td>
</tr>
<tr>
<td>$B$–$B$ Dissociation Energy</td>
<td>3.0 $\pm$ 0.5$^c$</td>
</tr>
<tr>
<td></td>
<td>3.6$^d$</td>
</tr>
<tr>
<td>$B$–$B$ $\Delta H_f$ (273 K)</td>
<td>4.987$^e$</td>
</tr>
<tr>
<td>$B$–$B$ Atomization Energy (in TiB$_2$)</td>
<td>5.814$^f$</td>
</tr>
<tr>
<td>$B$–$B$ $\Delta H_{bond}$ (2c-2e$^-$ in closo-$B_6H_6$)</td>
<td>3.4408$^g$</td>
</tr>
</tbody>
</table>

Table 7.14: Values related to $B$–$B$ bond strengths.
Figure 7.23: Morse Method I boron pair-potentials.
The $r_{eq}$ and $E_0$ are fixed to values obtained from lattice inversion.
Figure 7.24: Morse Method II boron pair-potentials. Parameters are relaxed to fit lattice energy.
Pair-potentials are good approximations for systems which have spherically symmetric interactions. As evidenced by the complex structures typically formed, this is not the case with boron. Directional bonding could be employed by the use of a Tersoff potential or some other bond-order scheme, but a simpler method is proposed here. As experimental evidence has shown [98], the intraoctahedral boron bonds are quite rigid. This leads one to believe that fixing the boron intraoctahedral spacings to their equilibrium distances is a plausible method for simulating this structure, as only small amounts of information will be lost. In this scenario, only the interoctahedral distances (those between the octahedra) will change, effectively treating the octahedral unit as a single rigid entity. The potential can thus be decomposed so that it only takes non-intraoctahedral interactions into account. This is illustrated in Fig. 7.25.

In order to fully characterize the non-equilibrium effects and restricted degrees of freedom for the rigid octahedra, the hexaboride units are also allowed to rotate during the fitting procedure. This helps to mimic actual octahedral configurations encountered during a MD simulation. Data is generated for a range of lattice constants with octahedral rotations of 0°, 10°, 20°, 30°, 40°, and 45° about the z-axis. A rotation of 45° reaches a symmetry point; therefore, a good portion of the single-axis rotational trajectories is sampled. Inclusion of these non-equilibrium states is important to stabilize the potential, as will be seen later, steering it away from developing wild fluctuations or abnormal minima in a dynamical setting.

To produce the potential required for this interaction, a set of lattices containing only boron is generated such that the $B_6$ octahedra are located at the center of a cubic lattice with intraoctahedral $B–B$ distances set to the equilibrium bond length for the $LaB_6$ structure ($B–B_{\text{eq \ intraO}_6} = 1.762 \, \text{Å}$). As the lattice constant and angles are var-
Figure 7.25: Lattice stretching and rotation of the $B - B_{\text{inter}O_h}$ bonds. Lattice constant changes and octahedra rotate while the intraoctahedral bond lengths are fixed to the equilibrium structure values.
ied, the energy changes are able to reflect the boron interactions between octahedral structural units. At large separations, when energy variations level out, the total energy for the unit cell is essentially the energy of a single octahedral unit interacting with itself (i.e., only composed of intraoctahedral interactions). Subtracting this isolated octahedral energy removes the lattice energy contributions associated with the $B - B_{\text{intra}O_h}$ potential, leaving only the interoctahedral interactions.

As a first approximation, the $B - B_{\text{inter}O_h}$ potential is assumed to be only between the first nearest-neighbors. Dividing the total normalized energy by six (so that the potential is for a single boron atom) and setting the interatomic distances to the nearest-neighbor interoctahedral bond lengths, a Morse potential is fit. This potential, based solely upon nearest-neighbor interactions, is given below as Morse$_{NN}$ in Fig. 7.26. DL_POLY, however, includes all neighbors for each of the boron atoms outside the fixed octahedra. Thus, every boron atom will interact with every other boron atom located in neighboring image cells. To produce a potential which accurately reflects this behavior, the Morse$_{NN}$ parameters are used as a first approximation to the actual parameters, and these are then relaxed using the $MII$ scheme.

Two sets of $MII$ parameters are generated to see the effect of the rotational energetics. “$MII$ (Equilibrium Configuration)” fits the potential to only the $0^\circ$-rotated lattice energy, neglecting all other rotations. “$MII$ (Rotational Perturbation)” includes all of the rotations within the set. These two are also depicted in Fig. 7.26.

The three Morse potentials are used to calculate the lattice energy for a boron octahedron system at both $0^\circ$ and $45^\circ$ rotations and illustrated in Fig. 7.27 and Fig. 7.28, respectively. Note that the lattice energy shown only reflects the contributions from $B_i - B_j$ interactions occurring outside the $i^{th}$ octahedron.

After reviewing Fig. 7.27 and Fig. 7.28, it should be evident why it was necessary to include the rotational perturbations. While the $MII$ (EC) potential is able to fit
Figure 7.26: Static $B - B_{\text{interO}_h}$ pair-potentials for a hexaboride lattice.
Figure 7.27: Calculated unit cell cohesive energy for a $0^\circ$ octahedral rotation.
Figure 7.28: Calculated unit cell cohesive energy for a 45° octahedral rotation.
the equilibrium lattice energy extremely well, the binding energy becomes far too strong when the system is allowed to rotate. This effect would act to stabilize the system out of equilibrium, trapping the hexaboride units in an unnatural state. The MII (RP) potential has a more compressed and deeper well, but it is able to produce the correct trends for lattice energies (since the 0°-rotated equilibrium configuration is has a lower energy value) in accord with the QUANTUM ESPRESSO data and experimental observation. Morse parameters for the three potentials are given below in Table 7.15. The minimized calculated lattice energies are given below in Tables 7.16 and 7.17 for the 0°-rotated and 45°-rotated lattices, respectively. These newer values of $E_0$ show a much better agreement with suggested bonding energies from Table 7.14.

<table>
<thead>
<tr>
<th>Curve</th>
<th>$r_{eq}$ (Å)</th>
<th>$E_0$ (eV)</th>
<th>$k_0$ (Å$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Morse$_{NN}$</td>
<td>1.6239</td>
<td>1.74875</td>
<td>1.3990</td>
</tr>
<tr>
<td>Morse Method II (EC)</td>
<td>2.0002</td>
<td>0.94625</td>
<td>1.6956</td>
</tr>
<tr>
<td>Morse Method II (RP)</td>
<td>1.6436</td>
<td>2.29836</td>
<td>2.5416</td>
</tr>
</tbody>
</table>

Table 7.15: Parameters for static $B-\text{B}_{\text{interO}_h}$ Morse potentials. EC = Equilibrium Configuration. RP = Rotational Perturbation.

7.5.6 Dynamic Interoctahedral Boron Potential

In addition to producing potentials which accurately reflect static data, it is important that the dynamics of the system are correct, especially for modeling transport properties. Up to this point, all of the potentials have had their parameters fit to static data. Although there is some flexibility in the models to handle non-equilibrium configurations, there is no certainty that the system will keep stability through thermal fluctuations. MSD’s can give insight into how the system is reacting to the strengths of the potentials under the influence of varying temperatures.
Table 7.16: Unit cell cohesive energy calculated from static $B - B_{\text{inter}O_h}$ potential fits and DFT data for a $0^\circ$ octahedral rotation. Note the close values of the interoctahedral distances for the QUANTUM ESPRESSO calculated values to the experimental $LaB_6$ $B - B_{\text{inter}O_h}$ distance. The experimental interpolation is a linear fit between $Nd$ and $Y$ hexaboride $B - B_{\text{inter}O_h}$ distances (relatively small ions), whose lattice constants bound the calculated value. EC = Equilibrium Configuration. RP = Rotational Perturbation. References: $a$ = [30], $b$ = [18].

<table>
<thead>
<tr>
<th>Curve</th>
<th>$a_{eq}$ (Å)</th>
<th>$\varepsilon_{min}$ (eV)</th>
<th>$B - B_{\text{inter}O_h}$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Morse$_{NN}$</td>
<td>3.3867</td>
<td>-41.433</td>
<td>0.8951</td>
</tr>
<tr>
<td>Morse Method II (EC)</td>
<td>4.1117</td>
<td>-10.524</td>
<td>1.6201</td>
</tr>
<tr>
<td>Morse Method II (RP)</td>
<td>4.0747</td>
<td>-9.9800</td>
<td>1.5831</td>
</tr>
<tr>
<td>QUANTUM ESPRESSO</td>
<td>4.1117</td>
<td>-10.492</td>
<td>1.6201</td>
</tr>
<tr>
<td>Experimental $LaB_6^a$</td>
<td>4.1569</td>
<td>—</td>
<td>1.6590</td>
</tr>
<tr>
<td>Experimental Interpolation$^{a,b}$</td>
<td>4.1117</td>
<td>—</td>
<td>1.6350</td>
</tr>
</tbody>
</table>

Table 7.17: Unit cell cohesive energy calculated from static $B - B_{\text{inter}O_h}$ potential fits and DFT data for a $45^\circ$ octahedral rotation. EC = Equilibrium Configuration. RP = Rotational Perturbation.

<table>
<thead>
<tr>
<th>Curve</th>
<th>$a_{eq}$ (Å)</th>
<th>$\varepsilon_{min}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Morse$_{NN}$</td>
<td>3.2280</td>
<td>-60.291</td>
</tr>
<tr>
<td>Morse Method II (EC)</td>
<td>3.7572</td>
<td>-15.255</td>
</tr>
<tr>
<td>Morse Method II (RP)</td>
<td>3.8630</td>
<td>-9.4807</td>
</tr>
<tr>
<td>QUANTUM ESPRESSO</td>
<td>3.9688</td>
<td>-7.6087</td>
</tr>
</tbody>
</table>
Therefore, the $B-B_{inter}O_h$ potential is adjusted so that it can reproduce dynamics within the temporal evolution of the system, producing a pairwise interaction for use with the dynamic set of potentials.

DL POLY is used to model the system at various temperatures and extract this dynamic data. Each MD run produces a HISTORY output file which is essentially a log of atomic coordinates, velocities, and forces for each atom and time step in the simulation [127]. These coordinates are used to calculate MSD values for each atom with the following relationship:

$$MSD(\tau) = \frac{1}{N_{atoms} \cdot t_{max}} \sum_i \sum_j (q_i(t_j + \tau) - q_i(t_j))^2$$  \hspace{1cm} (7.23)

In the above equation, $N_{atoms}$ is the number of atoms of a specific type within the system, $t_{max}$ is the number of allowed time steps to calculate a temporal difference, and $q_i$ is position of particle “i” at the specified time. After an equilibration run has been performed, the MSD values are calculated for every $\tau$ and temperature. These are then averaged for each atom type to give a single MSD value at a specified temperature. Using the calculated MSD$_{average}$ values from DL POLY for the temperature range, a sum-of-squares error between DFT- and MD-calculated MSD values can be used as an objective function to minimize, modifying the static DFT-derived potential to give the system a more reasonable dynamic behavior.

Since the calculated MSD values from QUANTUM ESPRESSO are close in proximity to experimentally realized displacements (shown in Fig. 6.8 and Fig. 6.9), they are taken as a reference point with temperatures of 100 $K$, 500 $K$, 900 $K$, and 1000 $K$ set as the targets to match. DL POLY runs are carried out at 10 atm for 5000 $fs$ with an equilibration period of 750 $fs$. An $8 \times 8 \times 8$ supercell of neutral boron octahedra interact via the Morse potential with radial cutoffs of 12 Å. MSD’s are then determined from these runs, taking the interval between 1 $ps$ and 5 $ps$ for calcula-
tion of averages on 2 ps blocks in order to mitigate possible deviations occurring on
the temporal boundaries.

Optimization is handled in a similar manner to MII. A set of 6 new potentials
is generated for each iteration, changing each parameter value by ±δ%, decreasing
the value of “δ” as the solution converges. Sum-of-squares errors are calculated for
each of the average MSD values within the set. An additional run is conducted
for a weighted set of parameter values, using the difference in the squared-error to
guide and speed up the process, computed with

\[
X_{i+1} = \begin{cases} 
\frac{\sigma_{\text{max}} - \sigma(X_i)}{\sigma_{\text{max}} - \sigma_{\text{min}}} (X_i - X_{i-1}) & \text{if } \sigma(X_i) < \sigma(X_{i-1}), \\
X_i & \text{if } \sigma(X_i) \geq \sigma(X_{i-1}).
\end{cases}
\]  

(7.24)

where σ is the sum-of-squares error between MD- and DFT-calculated MSD values
for the range of temperatures. Of the seven parameter sets tested, the values which
give the lowest squared-error are chosen for the next step, continuing this process
until a minimum is reached.

The relaxed parameters for the B–B_{inter}O_h dynamic potential are \( r_{eq} = 1.64607 \)
Å, \( E_0 = 4.2819 \) eV, and \( k_0 = 4.1625 \) Å\(^{-1}\). DL_POLY generated MSD’s, along with
their averages and the target DFT values, are shown in Fig. 7.29. Note that the
dissociation energy and exponential parameter have both increased, strengthening
the B–B bonds and reducing their degrees of freedom, while the equilibrium distance
has remained relatively unchanged. The weakness of the original MII (RP) bonds
gave rise to very large deviations, and the new energetics fall in the range expected
from values in Table 7.14.
Figure 7.29: MSD values for the boron interoctahedral potential. Average values for the initial and final parameter sets are compared to DFT data.
7.6 Lanthanum-Boron Interatomic Potential

As discussed earlier, the lanthanum hexaboride system is difficult to invert to produce either $B–B$ or $La–B$ interatomic potentials, owing to the complexity of the boron sub-lattice. To circumvent this issue, various schemes are implemented to produce a well-suited potential for this interaction. As a first approximation, the L1$_2$ structure is utilized, containing three boron atoms and a single lanthanum per unit cell. This is followed by translational perturbation methods similar in manner to how the $B–B_{interO_h}$ potential is developed, relaxing the Morse parameters to give a good fit to the lattice energy.

One element which has not been encountered yet in the development of homatomic potentials is the inclusion of electrostatics, since thus far there have been no separation of charges. When lanthanum and boron are in close proximity, electrons are donated from the lanthanum to the boron cage, producing additional electrostatic energies between all of the atoms. This could be handled by subtracting either a Coulomb potential or the energy from another electrostatic calculation, such as the smooth-particle-mesh Ewald method, but different approaches are used in this work which will be discussed in Sections 7.6.2 and 7.6.3.

7.6.1 Hypothetical L1$_2$ Lanthanum Triboride System

Although lanthanum and boron do not naturally form a L1$_2$ structure, insight may be gained from the interactions obtained through the inversion process. This structure, shown in Fig. 7.30, has $La$ at the simple cubic sites and $B$ at the anion sites. It bears a similar relationship to the lanthanum hexaboride system with a crystallographic refinement parameter of $\omega = 0$, though it should be obvious that there is a two-fold reduction in the number of anions.

To isolate the $La–B$ lattice potential, the $La–La$ and $B–B$ interactions were cal-
culated within DFT for their respective sub-lattices (La simple cubic and $B_3$ at the anionic positions) and subtracted, using the same vector of lattice constants. For an arbitrary system, the total potential can be decomposed as

$$E_{total}(a) = \phi_{La}^0 + \phi_{B}^0 + E_{La-La}(a) + E_{B-B}(a) + E_{La-B}(a) + E_{elec} \tag{7.25}$$

Note that this method ignores the possibility of electrostatics. The electrostatic energies have been calculated within DL_POLY for the same lattice constants, but removal of this energy produced unphysical results, possibly due to the assignment of an unrealistic set of charges.

Figure 7.30: Hypothetical lanthanum triboride $L1_2$ structure. Structure is similar to the face-centered cubic lattice, with lanthanum ions (yellow) at the corners and boron (fuschia) on the faces.

For the electrically neutral $L1_2$ system, $La-B$ interactions have been calculated
using both $MI$ and $MII$. The resulting pair-potentials are shown below in Fig. 7.31. Recalculated lattice energies are shown in Fig. 7.32. Important parameters and lattice energies for these functions are given below in Tables 7.18 and 7.19, respectively.

![Graph showing pair-potentials](image)

**Figure 7.31:** $La\text{–}B$ pair-potentials from the L1$_2$ structure.

<table>
<thead>
<tr>
<th>Curve</th>
<th>$r_{eq}$ (Å)</th>
<th>$E_0$ (eV)</th>
<th>$k_0$ (Å$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Morse Method I</td>
<td>3.3724</td>
<td>0.54478</td>
<td>1.3812</td>
</tr>
<tr>
<td>Morse Method II</td>
<td>3.3371</td>
<td>0.43630</td>
<td>1.1381</td>
</tr>
</tbody>
</table>

**Table 7.18:** Parameters for $La\text{–}B$ interatomic Morse potentials from $LaB_3$.

Unfortunately, the L1$_2$ inversions will not be of much use aside from giving a comparison to other derived energies. The complete neglect of electrostatic interactions forces the pairwise potential to have too deep of a well, as this attractive region is handled by the Coulomb potential. Abnormal electrostatic polarizations are also
Figure 7.32: Unit cell La–B cohesive energy for the L1\(_2\) structure.

<table>
<thead>
<tr>
<th>Curve</th>
<th>(a_{eq}) (Å)</th>
<th>(E_{min}) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Morse Method I</td>
<td>4.6422</td>
<td>-7.6222</td>
</tr>
<tr>
<td>Morse Method II</td>
<td>4.3505</td>
<td>-7.2746</td>
</tr>
<tr>
<td>Möbius Inversion</td>
<td>4.3829</td>
<td>-7.2295</td>
</tr>
<tr>
<td>QUANTUM ESPRESSO</td>
<td>4.3657</td>
<td>-7.2277</td>
</tr>
</tbody>
</table>

Table 7.19: Unit cell cohesive energy for \(LaB_3\) from inversions, potential fits, and DFT data.
produced in the DFT calculation due to the cation to anion ratios and incorrect assignment of charges. This could have negative effects on the stabilization energy for the system when applied to an actual $MB_6$ crystal.
7.6.2 La–B Translational Perturbations: Static Potential

The goal in this work is to create potentials which will correctly model the dynamics of a lanthanum hexaboride system at various temperatures, with and without applied external fields. In order to accomplish this task, it is important to sample the various structures we anticipated appear in these environments to be certain that their energetics are properly incorporated. As exemplified by the $B-B_{\text{inter}O_h}$ potential, neglecting the energies of non-equilibrium structures can have drastic results. It is expected that the lanthanum-boron distance will change in both symmetric and non-symmetric fashions about the equilibrium position during dynamic simulations, especially when electric fields are incorporated.

Two methods are employed to model the transient behavior of lanthanum within the lattice, each having its own merits. In each, translations of the lanthanum ion is modeled within DFT to produce lattice energies for the respective perturbations, and the boron octahedra are constrained to their equilibrium $B-B_{\text{intra}O_h}$ distances. The contrast lies in how electrostatics are handled.

The first scheme models lanthanum diffusing through the boron sub-lattice in a similar manner to how the real system would behave. Translations in the $x$-direction are allowed until the ion reaches the symmetry point at 50% of the lattice constant. This is anticipated to produce configurations observed when external fields are applied, deterring unrealistic energetics during migration. This scenario is depicted in Fig. 7.33 below. Cation charges are set to +2 in this method, and the interaction is fit to a Morse potential. The choice of using a dication spurs from recent evidence that the “actual” charge on lanthanum is between +2 and +3 [22]. In addition, it is believed that the attractive energy well from the Morse potential will be able to capture higher multipole and polarization effects coming from the QUANTUM ESPRESSO calculations, effectively increasing the charge at shorter distances.
Figure 7.33: Horizontal migration of La through a fixed lattice. While keeping the boron octahedra fixed at their equilibrium $B-B_{\text{intraO}_h}$ bond lengths, lanthanum is allowed to move in the $x$-direction for various lattice constants.

To extract the $La-B$ interaction energy, DFT-calculated lattice energies of the $La$ and $B$ substructures are removed from the total energy to give

$$E_{La-B}(a) + E_{\text{elec}}(a) = E_{\text{total}}(a) - \left( \phi_{La}^0 + \phi_B^0 + E_{La-La}(a) + E_{B-B}(a) \right)$$ (7.26)

The resulting potential contains only the $La-B$ van der Waals interaction and electrostatics. Since we are using DL_POLY to carry out MD simulations, this program is used to produce electrostatic energies for each of the simulated lattices. The idea behind using MD-calculated electrostatics is that these are the exact same values which will be included when running dynamic simulations, allowing the fully quantum energy to be reproduced and help connect the DFT-derived potentials with MD-calculated energies. To calculate the electrostatic potentials, an $8 \times 8 \times 8$ supercell is generated and simulated for a single time step with charges set for a lanthanum dication. The van der Waals forces are turned off, allowing only electrostatic forces to be computed with the smooth-particle mesh Ewald method ($10^{-8}$ precision). The
electrostatic energy is then removed, resulting in the $La-B$ van der Waals contributions to the lattice energy, $E_{La-B}(a)$. The $La-B$ van der Waals lattice energies for a $La^{+2}$ system are shown below in Fig. 7.34, normalized to the cut-off energy for lanthanum in its equilibrium position. Truncating the potential at this point is chosen since the equilibrium structure is generally taken as a reference point.

Two things should be apparent about the curves found in Fig. 7.34: (1) the minimum energy decreases as lanthanum migrates through the lattice and (2) they are cut off at different distances. Both of these effects have to do with the long-range nature of electrostatic energies and neglect of polarization. As one can see from any of the lattice energies for neutral systems, the variations in energy quickly die out and converge to a constant value. Depending on the charges involved, electrostatic po-
tentials for point charges typically do not converge until a very large lattice constant is reached. The curves in Fig. 7.35 show the extracted migration lattice energies \((E_{La-B} + E_{elec})\) along with an average of the DL_POLY-derived electrostatic potential (\(n.b.,\) the electrostatic energies differed by at most 3% at the smallest lattice constant, making the average a good representation for illustration purposes).

\[
\begin{align*}
&\text{Left Axis: Lattice energies formed by subtracting the La–La and B–B lattices.} \\
&\text{Right Axis: Average DL_POLY derived electrostatic energies for LaB}_6.
\end{align*}
\]

Notice that the minima of the lattice energies for each perturbation are located at different lattice constants. These will be shifted by different amounts when the electrostatic energy is removed. This is the reason for the large deviations between the magnitude of the energies in Fig. 7.34.

To address the variations in potential cut-offs, notice that while the lattice energies level out, the electrostatic contribution is still increasing. This would have the effect of producing a sigmoidal-shaped lattice energy, where the saddle-point lies
around the lattice energy minimum. In a higher-level simulation, such as DFT, the charges on atoms are fluctuating and depend on the orbitals and distances between atoms. Atoms in ionic systems would tend to be neutral at large separations and highly polarized at close distances. Since the $La-B$ potential should only be a short-ranged repulsive force with the majority of interaction due to Coulombic attraction, the potentials are therefore truncated at the top of the saddle point just before it returns on a downward path. This avoids the problem of dealing with an unrealistic potential.

The extracted $\varepsilon_{La-B}$ energies are used with $MII$ to fit a Morse potential over all lanthanum translations and lattice constants. This resulting function had the correct characteristics of a repulsive van der Waals force and a much shallower energy well than the L1$_2$ potentials, shown below in Fig. 7.36. Unfortunately there is no comparison as none of the other potentials account for electrostatics. However, lattice energies with electrostatic contributions were computed for each of the translational steps and lattice constants, illustrated in Fig. 7.37. The energies are only given up through the cut-off values employed for the calculation, but the curves have the same general shape and increase in energy as migration proceeds. Parameters for the $MII$ $La-B$ potential are given in Table 7.20 and a comparison of the energy minima for the QUANTUM ESPRESSO data and recalculated lattice energies can be found in Table 7.21. Note that although there is a shift in the lattice energy, the equilibrium lattice constants are in close proximity to the actual DFT-derived values and follow the correct trends.

<table>
<thead>
<tr>
<th>Curve</th>
<th>$r_{eq}$ (Å)</th>
<th>$E_0$ (eV)</th>
<th>$k_0$ (Å$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Morse Method II</td>
<td>4.1541</td>
<td>0.07868</td>
<td>1.0438</td>
</tr>
</tbody>
</table>

Table 7.20: Parameters for lanthanum-boron interatomic van der Waals Morse potentials from $LaB_6$. 
Figure 7.36: La–B van der Waals Morse potential.
The interaction between lanthanum and boron is essentially repulsive when the attractive electrostatics are removed.

<table>
<thead>
<tr>
<th>$La^{+2}$ % Migration</th>
<th>$a_{eq}$ (Å)</th>
<th>$E_{min}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>(4.3922, 4.3922)</td>
<td>(-7.6795, -8.7266)</td>
</tr>
<tr>
<td>10</td>
<td>(4.4980, 4.4451)</td>
<td>(-7.5835, -8.6444)</td>
</tr>
<tr>
<td>20</td>
<td>(4.6568, 4.6568)</td>
<td>(-7.2955, -8.2166)</td>
</tr>
<tr>
<td>30</td>
<td>(4.9213, 4.8684)</td>
<td>(-7.2378, -8.0026)</td>
</tr>
<tr>
<td>40</td>
<td>(5.0801, 5.0272)</td>
<td>(-7.2753, -7.7732)</td>
</tr>
<tr>
<td>50</td>
<td>(5.0801, 5.0801)</td>
<td>(-7.2393, -7.4882)</td>
</tr>
</tbody>
</table>

Table 7.21: Unit cell lattice energies for $LaB_6$ from potential fits and DFT data. Values are given as (QUANTUM ESPRESSO, MII-Calculated).
Figure 7.37: Calculated $La-B$ unit cell lattice energies ($E_{La-B} + E_{elec}$). Comparison with Fig. 7.35 shows good agreement between the two sets of curves.
One final step is introduced to produce a set of static potentials to match MSD values. Up until now, the three potentials used for static interactions — $La-La$ ($MII$, SC), $B-B_{interO_h}$ ($MII$, RP), and $La-B$ ($MII$, $LaB_6$) — have been strictly modeled against equilibrium quantum mechanical data. To be sure that the dynamics of the system are well-behaved, the three potentials are placed in a MD framework and matched to DFT-calculated MSD’s. The $B-B_{interO_h}$ potential is chosen as the interaction to be modified due to its weak interaction energy. Important input parameters for the DL_POLY simulation are given in Table 7.23. After relaxing the boron homatomic potential, the dynamic behavior of the system gave good agreement with DFT for MSD’s. The three static parameters are shown below in Table 7.22 and the resulting MSD’s for boron and lanthanum can be found under the heading MD Relaxed in Fig. 7.38 and Fig. 7.39, respectively.

<table>
<thead>
<tr>
<th>Interaction</th>
<th>$La$ Charge</th>
<th>Potential</th>
<th>$r_{eq}$ (Å)</th>
<th>$E_0$ (eV)</th>
<th>$k_0$ (Å$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$La-La$</td>
<td>+2</td>
<td>Morse</td>
<td>4.2303</td>
<td>0.37130</td>
<td>0.8634</td>
</tr>
<tr>
<td>$B-B$</td>
<td>+2</td>
<td>Morse</td>
<td>1.5302</td>
<td>2.49361</td>
<td>2.6377</td>
</tr>
<tr>
<td>$La-B$</td>
<td>+2</td>
<td>Morse</td>
<td>4.1541</td>
<td>0.07868</td>
<td>1.0438</td>
</tr>
</tbody>
</table>

Table 7.22: Finalized static parameters for interatomic Morse potentials. Mean-square displacements at $T=100 \, K$, $500 \, K$, $900 \, K$, and $1000 \, K$ were used to fit the $B-B_{interO_h}$ potential to account for the system’s dynamic response.
Figure 7.38: Boron MSD values with finalized static parameters (DL_POLY). Comparison of initial and finalized parameters from the relaxation process. MSD’s are calculated with a step size of 10 fs, origin interval of 10 fs, and 2 ps blocks from a 10 ps run.
Figure 7.39: Lanthanum MSD values with finalized static parameters (DL_POLY). Comparison of initial and finalized parameters from the relaxation process. MSD's are calculated with a step size of 10 fs, origin interval of 10 fs, and 2 ps blocks from a 10 ps run.
<table>
<thead>
<tr>
<th>MD Parameter</th>
<th>Units</th>
<th>Static Potential</th>
<th>Dynamic Potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure</td>
<td>atm</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Integrator</td>
<td>—</td>
<td>Velocity Verlet</td>
<td>Velocity Verlet</td>
</tr>
<tr>
<td>Ensemble</td>
<td>—</td>
<td>NVT Hoover</td>
<td>NVT Hoover</td>
</tr>
<tr>
<td>$\Delta t_{step}$</td>
<td>$fs$</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Total Simulation Time</td>
<td>$ps$</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Equilibration</td>
<td>$fs$</td>
<td>1000</td>
<td>1000</td>
</tr>
<tr>
<td>$r_{cut}$</td>
<td>Å</td>
<td>12</td>
<td>12</td>
</tr>
<tr>
<td>SPME Precision</td>
<td>—</td>
<td>$10^{-8}$</td>
<td>$10^{-8}$</td>
</tr>
<tr>
<td>Number of Unit Cells</td>
<td>—</td>
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<td>512</td>
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<tr>
<td>Grid</td>
<td>—</td>
<td>$8 \times 8 \times 8$</td>
<td>$8 \times 8 \times 8$</td>
</tr>
<tr>
<td>Lattice Constant</td>
<td>Å</td>
<td>4.154</td>
<td>4.154</td>
</tr>
<tr>
<td>$\omega$</td>
<td>—</td>
<td>0.2001</td>
<td>0.2001</td>
</tr>
<tr>
<td>La Cation Charge</td>
<td>$e$</td>
<td>+2</td>
<td>+3</td>
</tr>
<tr>
<td>Rigid Octahedra</td>
<td>—</td>
<td>Yes</td>
<td>Yes</td>
</tr>
</tbody>
</table>

Table 7.23: Parameters for MSD fitting procedure.
7.6.3 La–B Translational Perturbations: Dynamic Potential

To obtain the dynamic heteroatomic potentials, an alternative scheme was used to handle electrostatics. Keeping the lattice constant and $B-B_{\text{inter}O_h}$ bonds fixed, the lanthanum cation was allowed to migrate toward the center of an octahedral face, traveling on a path normal to the plane created by the three boron atoms. Without significant variations in interatomic distances due to lattice stretching, the electrostatics should be fairly well-behaved. Thus, the lattice energy fluctuations that arise from this perturbation are assumed to be largely due to the van der Waals interaction between lanthanum and the octahedral face. A depiction of this process is shown in Fig. 7.40 and the lattice energies are given in Fig. 7.41.

![Figure 7.40: Diagonal translation of La through a fixed lattice. All atomic coordinates remain unchanged except for the lanthanum ion.](image)

Obviously the hard-sphere repulsion would prevent lanthanum from fully migrating through the octahedron, but it is instructive to note the limitations of DFT. To keep in accord with developing a strictly repulsive van der Waals interaction, the lattice energies are truncated just below the inflection point, where lanthanum is located 0.8994 Å from the center of the octahedron. An initial fit is produced, assum-
Figure 7.41: Lattice energy changes for diagonal lanthanum translation. All atomic coordinates remain unchanged except for the lanthanum ion.
ing lanthanum interacts solely with the three borons comprising the face normal to the migration path. Using this potential as a basis for the MII optimization, the lattice energy is fit to a Buckingham exp-6 potential for all La–B interactions up to the 12 Å cut-off value. The relaxed potential is shown in Fig. 7.42 and the recalculated lattice energies for the diagonal translation are compared with the QUANTUM ESPRESSO data in Fig. 7.43. The lattice energy computed from the Buckingham potential gives rise to a residual energy of 2.616 eV at the lanthanum equilibrium position. However, the curvature of the model should allow for appropriate interactions between the two types of atoms. Parameters obtained for the Buckingham potential are \( A = 1374.4824 \text{ eV}, \rho = 0.3228 \text{ Å}, \) and \( C = 0. \)

Armed with decent parameters for all three dynamic potentials, DL_POLY is again utilized to incorporate MSD values for fine-tuning. Inputs to the CONTROL
Figure 7.43: Calculated lattice energies for diagonal lanthanum translation.
file for the MD simulation are given in Table 7.23. Both the $B-B_{\text{interO}}$ and $La-B$ interactions are optimized to give the relaxed parameters for the dynamic potential. The finalized parameter values can be found in Table 7.24, along with some published $La^{\text{+3}}$ potentials found in the literature. Fitted MSD’s from the final iteration for boron and lanthanum are shown in Fig. 7.44 and Fig. 7.45, respectively.

<table>
<thead>
<tr>
<th>Interaction</th>
<th>$La$ Charge</th>
<th>Potential</th>
<th>$r_{eq}$</th>
<th>$E_0$</th>
<th>$k_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$La-La$</td>
<td>+3</td>
<td>Morse</td>
<td>4.2328</td>
<td>0.58706</td>
<td>1.2162</td>
</tr>
<tr>
<td>$B-B$</td>
<td>+3</td>
<td>Morse</td>
<td>1.6645</td>
<td>4.30396</td>
<td>4.1918</td>
</tr>
<tr>
<td>$La-B$</td>
<td>+3</td>
<td>Buckingham</td>
<td>0.37308</td>
<td>1524.91</td>
<td>0</td>
</tr>
<tr>
<td>$La$ in ionic oxide $^a$</td>
<td>+3</td>
<td>Buckingham</td>
<td>0.3651</td>
<td>1439.7</td>
<td>0</td>
</tr>
<tr>
<td>$La$ in $La_2NiO_4$ $^b$</td>
<td>+3</td>
<td>Buckingham</td>
<td>0.3590</td>
<td>1545.21</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 7.24: Finalized dynamic parameters for interatomic Morse and Buckingham potentials.
Morse parameters: $r_{eq}$, $E_0$, and $k_0$. Buckingham parameters: $\rho$, $A$, and $C$. References: $a = [82]$, $b = [96]$. 
Figure 7.44: Boron MSD values with finalized dynamic parameters (DL_POLY). Comparison of initial and finalized parameters from the relaxation process. MSD’s are calculated with a step size of 10 fs, origin interval of 10 fs, and 2 ps blocks from a 10 ps run.
Figure 7.45: Lanthanum MSD values with finalized dynamic parameters (DL_POLY).
Comparison of initial and finalized parameters from the relaxation process. MSD’s are calculated with a step size of 10 fs, origin interval of 10 fs, and 2 ps blocks from a 10 ps run.
Chapter 8

Classical Molecular Dynamics of LaB$_6$

8.1 Simulation Box and Setup

The periodic system employed in DL_POLY consists of an $8 \times 8 \times 8$ supercell containing 512 lanthanum ions and 3072 boron atoms, shown for reference in Fig. 8.1. The geometry of the system is defined in the CONFIG file, and a truncated version of this is given in Appendix B.3. Minimized lattice energies determined from QUANTUM ESPRESSO produce $a = 4.154$ Å and $\omega = 0.2001$, and the superlattice is generated according to these parameters.

Environmental variables such as electrostatics, temperature, pressure, thermostats, barostats, integrators, and various program controls are each set according to their desired values in the CONTROL file (see Appendix B.2). The Velocity-Verlet algorithm is chosen to integrate the canonical system, controlled by a Nosè-Hoover thermostat with a coefficient of 0.5. Electrostatics are carried out using the smooth-particle-mesh Ewald method with a precision of $10^{-8}$. Radial cutoffs of 12 Å are set in accordance with the development of the pair-potentials. A pressure of 10 atm is
Figure 8.1: Lanthanum hexaboride simulation box used in DL_POLY. A total of 512 $LaB_6$ unit cells are arranged in a periodic box having a length of 33.232 Å per side.
used for all simulations and temperatures are kept as a parameter for modeling.

Interatomic interactions are prescribed in the FIELD file (Appendix B.1), which allows one to choose from various potentials and parameters. The static and dynamic potentials derived in Chapter 7 are implemented, with boron charges set to give neutrality. Hexaboride units are kept as discrete rigid systems, allowing rotational motion but keeping $B-B_{\text{intra}O_b}$ distances fixed.

### 8.2 Temperature Effects without External Fields

The lanthanum hexaboride system described above is simulated for temperatures at $50 \, K$ and between $100 \, K$ and $1000 \, K$ at intervals of $100 \, K$. Simulations are run for a total of $20 \, ps$ including a $1000 \, fs$ equilibration period. An additional picosecond is removed after equilibration for MSD calculations, giving the system further opportunity to mitigate post-equilibration effects from removal of the constraints. MSD values for each of the atoms are calculated for the static and dynamic parameter sets over the 18 picosecond range, using sample and origin intervals of $10 \, fs$ with array lengths set to $5 \, ps$. Averages are shown below for boron and lanthanum using the static set in Fig. 8.2 and Fig. 8.3, respectively, with experimental results obtained by Booth et. al. [19] and DFT-calculated values given for reference.

It appears that the static dication system reproduces the MSD trends fairly well for the octahedra, though the curve drops off faster in the low temperature range. It is expected that the borons should have a lower range of motion since some of the degrees of freedom have been removed. Lanthanum seems to be much more constrained in the high temperature range, suggesting the heteroatomic potential may be too strong and restricting motion. Overall, the static potential performs well at describing the dynamics of the crystal at varying temperatures, keeping the DFT-derived MSD’s within error bounds at reasonable temperatures.
Figure 8.2: Boron mean-square displacements from static potentials. Average values are taken from the interval between 2 ps and 20 ps during the DL_POLY simulation. Error bars represent standard deviations.
Figure 8.3: Lanthanum mean-square displacements from static potentials. Average values are taken from the interval between 2 ps and 20 ps during the DL_POLY simulation. Error bars represent standard deviations.
The boron and lanthanum MSD values for the dynamic potentials are shown in Fig. 8.4 and Fig. 8.5, respectively, again with experimental and DFT data. Both lanthanum and boron MSD’s seem to reasonably fit the DFT data, although a slightly nonlinear relationship is observed, dropping off in the high temperature regions. This could possibly be due to the use of non-equilibrated data sets for the fitting process, requiring larger simulation times before a steady state has been reached. Another prospect is that the assigned charges are too large, producing stronger electrostatic interactions which dampen the system’s dynamics. This would explain the tendency of the atoms to be constricted at elevated temperatures. The assumption that lanthanum loses its entire valence set is unlikely, as the boron framework only demands two electrons per unit cell to fulfill its orbital requirements. In some cases, a single electron will suffice, as evidenced by the formation of potassium hexaboride. Thus, it is plausible that a fractional charge or polarizable field would be better suited to describe heteroatomic interactions within this compound.
Figure 8.4: Boron mean-square displacements from dynamic potentials. Average values are taken from the interval between 2 ps and 20 ps during the DL_POLY simulation. Error bars represent standard deviations.
Figure 8.5: Lanthanum mean-square displacements from dynamic potentials. Average values are taken from the interval between 2 ps and 20 ps during the DL_POLY simulation. Error bars represent standard deviations.
8.3 Ionic Transport

The same superlattice described above is also used to simulate the effects of an added external electric field. However, it was found that application of the field would place similar migratory effects on the boron sub-lattice; therefore, restrictions were placed on their positions to keep the system intact. Two different constraints were implemented, giving the octahedra varying levels of degrees of freedom. Temperatures were ranged from 20 \text{ K} to 1900 \text{ K} to see the effects of boron's vibrational freedom on diffusion. Simulations are set up such that the system has time to equilibrate prior to application of the field. An equilibration period of 1 ps is followed by an additional picosecond after the constraints are removed. The electric field is then applied, with field forces ranging from null to 3.2 V/(Å · e), and the system is allowed to progress for 8 ps before analysis. All other parameters aside from the electric field are identical to those given for the equilibrium simulation. The first 3 ps are trimmed prior to analysis, allowing the system to relax into its new state after application of the field. MSD sample and origin intervals and are 10 fs with array lengths of 3.5 ps.

8.3.1 Fixed Lattice

In one scenario, the entire boron framework was completely immobilized in space. This allows one to determine an upper limit on the electric field strengths required for electrodiffusion to occur. Without the ability of the octahedron to expand and contract, activation energies for the migratory process are elevated. Results for this process are shown below in Fig. 8.6 and Fig. 8.7 for the static potentials. The dynamic potentials are given in Fig. 8.8 and Fig. 8.9.

The graphs show the spectrum of particle frequencies on the left side and the mean-square displacements on the right side for lanthanum. The frequencies are only shown for those temperatures in which the system has not yet begun to diffuse.
Figure 8.6: La oscillation frequencies and MSD’s with applied electric field in a fixed lattice for static potentials (I).

Left: Main contributions to the frequency spectrum. Oscillations are only shown for atoms which have not yet begun to diffuse. Right: Mean-square displacements of lanthanum (window fit to largest value).
Figure 8.7: La oscillation frequencies and MSD’s with applied electric field in a fixed lattice for static potentials (II).

Left: Main contributions to the frequency spectrum. Oscillations are only shown for atoms which have not yet begun to diffuse. Right: Mean-square displacements of lanthanum (window fit to largest value).
Figure 8.8: $\text{La}$ oscillation frequencies and MSD's with applied electric field in a fixed lattice for dynamic potentials ($I$).

**Left:** Main contributions to the frequency spectrum. Oscillations are only shown for atoms which have not yet begun to diffuse. **Right:** Mean-square displacements of lanthanum (window fit to largest value).
Figure 8.9: \( \text{La} \) oscillation frequencies and MSD's with applied electric field in a fixed lattice for dynamic potentials (II).

*Left:* Main contributions to the frequency spectrum. Oscillations are only shown for atoms which have not yet begun to diffuse. *Right:* Mean-square displacements of lanthanum (window fit to largest value).
The MSD's are displayed for the largest values; therefore, the temperatures at which diffusion has occurred can be clearly seen.

In both sets of potentials, one can observe a significant change in the distribution of frequencies as the electric field is increased. Just prior to diffusion, it appears that a single characteristic frequency is obtained for each of the temperatures. This may be due the electric field constraining the motion of the particles, or it could possibly be due to some set vibration energy modes required for this migratory process to occur. It is plausible that constructive interference of the phonons will give rise to a lower activation barrier for diffusion. However, further experimentation is required to definitively characterize this phenomena.

Electrodiffusion is observed to be initiated at $1500 \text{ K}$ and $1900 \text{ K}$ with a field strength of $2.2 \text{ V/Å}$ for both sets of potentials. Initially, in the static potential system, the system has a higher diffusion rate for a temperature of $1500 \text{ K}$. Whether this has to do with the vibrational set given by that specific temperature or an artefact of the computation will be handled through further experimentation in future work.

At the top end of the field strengths, the trication system has a much larger set of temperatures in motion, as should be expected. The force per particle is based upon the cation charge, so the dynamic potentials would be pushed by a force 50% higher than the dication system.
8.3.2 Half-Fixed Lattice

In the next set of simulations, every other octahedron is fixed in space such that no nearest-neighbor octahedra are both fixed or free, isotropically constraining the system. In this way, some of the borons are still able to vibrate around their equilibrium positions while still keeping the entire boron framework from migrating. It is expected that this additional range of motion should produce migration at much lower temperatures and field strengths than the fully fixed system. Since part of the boron sub-lattice has extra degrees of freedom, the cross-sectional area normal to the path that lanthanum must migrate through will now fluctuate, allowing for larger $La$–$B$ distances and thus lower energy barriers to overcome. Results for the static potential set are displayed in Fig. 8.10 and Fig. 8.11. Electric field effects for the dynamics potentials can be seen in Fig. 8.12 and Fig. 8.13.

Once again, the frequency distributions are altered by electric field for the “half-fixed” lattice systems. Owing to the motion of the octahedra, these frequencies are much less ordered, though they still tend to cluster around a specific set of vibrational modes.

Diffusion is observed at a field strength of 3.0 V/Å with temperatures of 300 $K$ and 500 $K$ for the static potentials. In fact, diffusion had occurred at much lower strengths, but the combination of thermal energy and forces induced by the field destroyed the octahedral lattice, so these were not included. However, these low temperatures were not observed to allow for migration at all within the fully-fixed octahedral system, so the boron displacements do in fact play a role in the relative ease of migration.

Diffusion for the dynamic potential set occurs at a field strength of 1.8 V/Å and temperatures ranging from 900 $K$ to 1900 $K$. Similar to the static potential set within the fixed octahedral system, a lower temperature (1500 $K$) gave rise to larger
Figure 8.10: La oscillation frequencies and MSD’s with applied electric field in a partially fixed lattice for static potentials (I).

*Left:* Main contributions to the frequency spectrum. Oscillations are only shown for atoms which have not yet begun to diffuse. *Right:* Mean-square displacements of lanthanum (window fit to largest value).
Figure 8.11: $La$ oscillation frequencies and MSD’s with applied electric field in a partially fixed lattice for static potentials (II).

Left: Main contributions to the frequency spectrum. Oscillations are only shown for atoms which have not yet begun to diffuse. Right: Mean-square displacements of lanthanum (window fit to largest value).

Figure 8.12: La oscillation frequencies and MSD’s with applied electric field in a partially fixed lattice for dynamic potentials (I).

Left: Main contributions to the frequency spectrum. Oscillations are only shown for atoms which have not yet begun to diffuse. Right: Mean-square displacements of lanthanum (window fit to largest value).
Figure 8.13: La oscillation frequencies and MSD’s with applied electric field in a partially fixed lattice for dynamic potentials (II).

Left: Main contributions to the frequency spectrum. Oscillations are only shown for atoms which have not yet begun to diffuse. Right: Mean-square displacements of lanthanum (window fit to largest value).
migrations. As the collective motions of the lanthanum within the lattice can produce stronger kinetic energies (similar to how constructive interference of waves gives rise to larger waves), it is possible that a specific set of temperatures and field strengths exist which decrease the activation barrier for this process. Stronger fields again placed the higher temperature sets with larger diffusion rates. It should be noted that the $B–B$ potential was strong enough in the dynamic set to resist lattice degradation in all tested environments.
Chapter 9

Concluding Remarks and Future Work

9.1 Conclusions

The combination of DFT and MD has proven to be a powerful tool in the design of novel interatomic potentials for this highly specialized system. Utilizing only high-level \textit{ab initio} calculations coupled with MD, we have developed two sets of pair-potentials which are able to reproduce equilibrium data fairly well, prescribing the atoms their correct motions within the lattice at specified temperatures. In addition, these have allowed for testing of this ceramic within an extremely non-equilibrium system under electric fields. Migration of the cations was observed to occur above electric field strengths of 2.2 V/Å in the fully-constrained octahedral system for both sets of potentials. Relaxing these constraints to give the boron atoms additional degrees of freedom let this migratory process to be achieved at lower fields, suggesting that motion of the octahedral framework is crucial to lowering these activation barriers. The dynamic potential set produced migration with $E = 1.8$ V/Å, about 20% lower than fully-constrained system. Reducing the amount of fixed octahedra should
give further reductions in the required forces, though the boron potentials would need to be stronger to resist structural deformation. Although the field strengths required to induce migration are on the higher-end, the potentials used are very simplistic. Better refinement of the potentials should allow for a more accurate model to be tested and analyzed.

In addition to finding that applied fields can induce ion migration at reasonable temperatures, a novel effect was observed to occur in this diffusive process. Oscillation frequencies of the cations show significant alterations as field strengths are increased and migratory behavior is approached. There are several possibilities as to why these occur – two are discussed here. The first is that the field forces the atoms in a specific trajectory set and dampens oscillations normal to the field direction. This would have the effect of constraining the frequencies to a specific subset. Another alternative is that these frequencies give the correct energetics for diffusion; therefore, as the environmental conditions approach those required to begin migration, the frequency sets evolve to show this behavior.

A strange result that occurred in some of these systems is that the highest temperatures, and therefore highest kinetic energies, were not the first to initialize migration. It is speculated that certain combinations of atomic velocities and field strengths can efficiently allow cation transport to occur. Each temperature will give rise to different vibrations of the atoms, and these vibrations are altered by the electric field. Specific frequencies arise as the cations are forced in one direction by the field and the reverse direction by their interaction with the octahedral lattice, bouncing back and forth between the two potentials. It is possible that a combined effect resulting from a specific temperature and field strength will give rise to constructive interference of the phonons, producing increasing amplitudes which eventually break the diffusive barrier.
9.2 Future Work

After laying the groundwork and getting initial data on this system, there are many improvements to the model which can be made. To start, the system is described by a set three simple pairwise potentials. These completely neglect third- and higher-body interactions, atomic polarization, and any contributions arising from the intraoctahedral bonds. Thus, they comprise a minimal set needed to describe this system. Inclusion of Tersoff-type potentials may improve the dynamics of the octahedral structures and stabilize the system further.

The simulations carried out do not include any method for handling electronic transport through the system aside from the effect on ion migration. In addition, the neglect of Joule heating (through the use of a thermostat) has important consequences, possibly producing incorrect phenomena in this highly idealized framework. These effects will also be tackled in further studies by this group.

The handling of electrostatics has been quite elementary in nature thus far. Charge density distributions will be studied to give a better description of how the electron clouds are distorted with both atomic movement and electronic fields. Analysis of electron localization functions through static perturbations and Car-Parrinello MD will give further insight into how the density is distributed in various environments, including external fields. The use of a “shell” model would help to incorporate these effects in a MD framework. These analyses should also aid in describing the $La-B$ potential much more accurately, allowing the polarization to decrease the current level of repulsion encountered.

Relaxation of the parameters by MD with much larger data sets (in terms of simulation times) will give a much better fit to equilibrium MSD’s. Algorithmic improvements will decrease the time required to calculate these, producing results in hours rather than days. With correct charge assignments, the correct shape of
these curves can also be obtained and fit to DFT data more precisely.

In addition, further experimentation and development of potentials will proceed to include other metal hexaborides and the effects of dopants and vacancies on migration. Insertion of hydrogen into the evacuated boride lattice is a crucial step, as this type of system is the final configuration we would like to attain. Once a suitable framework has been developed to properly handle these phenomena, the metal hexaboride lattice will be subjected to both electric and pressure gradients, observing cation diffusion and possibly hydrogen adsorption into the boron framework.

This work has initiated the study of hexaborides in a dynamic framework. Potentials have been developed for the first time to describe this system in static and dynamic environments within MD. Additional experimentation and testing will only produce a more accurate description of this system, aiding both theoretical and experimental work in this area.
References


[111] J.M. Prausnitz, R.N. Lichtenthaler, and E.G. de Azevedo. \textit{Molecular thermo-
dynamics of fluid-phase equilibria. Prentice Hall, New Jersey, 1999. 54, 57, 73, 80, 83


Appendix A

QUANTUM ESPRESSO Input Files
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  outdir = '$TMP_DIR/
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  celldm(1) = 7.85,
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B  0.7999  0.5000  0.5000
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A.3 QHA & DOS Files

A.3.1 Displacement.in

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  10.8110

A.3.2 fqha.in

PHDOS.out
lab6-03.QHA.out
5 1000 5

A.3.3 phdos.in

0.75
La B1 B2 B3 B4 B5 B6

A.3.4 T_Debye.in

PHDOS.out
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  3 15 3
  1000 5

A.3.5 matdyn.in

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   amass(2)=10.811,
   asr='simple',
   flfr=lab6-03.444.fc',
   flfrq='frequency'
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Appendix B

DL_POLY Input Files
B.1 FIELD File

FIELD File for LaB6 Simulations – UNR, 2014

UNITS eV
MOLECULES 2

OctaB6
NUMMOLS 512
ATOMS 6
# Rigid Octahedral Boron Structures
B 10.811000 -0.5 6 0
rigid 1
6 1 2 3 4 5 6
FINISH

LaIon
NUMMOLS 512
ATOMS 1
La 138.90547 3.0 1 0
FINISH

VDW 3
# Morse Parameters (E0, r0, k)
B B mors 0.3633 2.2166 1.5276
La B mors 0.5859 3.0542 1.6835
La La mors 0.2864 4.1569 1.0637

# External Electric Field
extern
elec 1 0 0
CLOSE
B.2 CONTROL File

CONTROL File for LaB6 Simulations - UNR, 2014

# System state information; T(K), P(katm)
temperature 500.00
pressure .01

# Integration and Ensemble Specification
integrator verlet velocity
ensemble nvt hoover 0.5

# Specify HISTORY file Printing
trajectory 0 10 0

# Simulation Controls
timestep 0.001
steps 5000
equilibration 500
multiple step 1
scale 10
print 10
stack 100
stats 10

# Force cut-offs and controls
cutoff 12 Angstroms
rvdw cutoff 12 Angstroms
delr width 0.01

# SPME Electrostatics
spme precision 1d-8

# Job Running and Closedown Time
job time 4000.00
close time 20.00

finish
### B.3 CONFIG File

LaB6 - Lattice Constant: 4.154 Angstroms

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