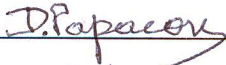
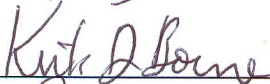
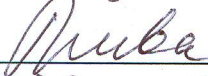
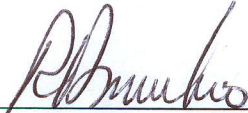
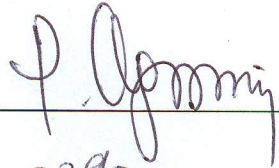


ELECTRONIC STRUCTURE AND MOLECULAR DYNAMICS SIMULATIONS
FOR ALKALINE EARTH AND ALKALI METALS

by

Mazhalai Chellathurai
A Dissertation
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of
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of
Doctor of Philosophy
Computational Sciences and Informatics

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Dedication

To
Amma and Appa,
Thinesh and Neyan

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Abbreviations

APW	Augmented Plane Wave.
Ba	Barium.
bcc	body centered cubic.
Ca	Calcium.
Cs	Xesium.
DFT	Density Functional Theory.
dia	diamond.
DLS	Damped Least Squares.
DOS	Density of States.
EAM	Embedded Atom Method.
fcc	face centered cubic.
FP	Full Potential.
GGA	Generalized Gradient Approximation.
hcp	hexagonal close packed.
K	Potassium.
LAPW	Linear Augmented Plane Wave.
LCAO	Linear Combination of Atomic Orbitals.
LDA	Local Density Approximation.
Li	Lithium.
LMA	Levenberg-Marquardt Algorithm.

LMTO	Linear Muffin-Tin Orbitals.
MD	Molecular Dynamics.
Mg	Magnesium.
MPI	Message Passing Interface.
MSD	Mean Square Displacement.
MTA	Muffin-Tin Approximation.
MTO	Muffin-Tin Orbitals.
Na	Sodium.
NRL	Naval Research Laboratory.
Rb	Rubidium.
RPA	Random Phase Approximation.
Ry	Rydberg.
sc	simple cubic.
SK	Slater-Koster.
Sr	Strontium.
TB	Tight-Binding.
TBMD	Tight-Binding Molecular Dynamics.
VFE	Vacancy Formation Energy.

Abstract

ELECTRONIC STRUCTURE AND MOLECULAR DYNAMICS SIMULATIONS FOR ALKALINE EARTH AND ALKALI METALS

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George Mason University, 2013

Dissertation Director: Dr. Dimitrios Papaconstantopoulos

The Naval Research Laboratory (NRL) Tight-Binding (TB) method, which was introduced by Cohen, Mehl, and Papaconstantopoulos [1], was applied successfully to all transition and noble metals by the same authors in 1996 [2]. In this work, the NRL-TB method has been applied for the alkaline earth metals Strontium (Sr) and Calcium (Ca), for which the authors of [2] had mixed success, and for the alkali metals Rubidium (Rb) and Lithium (Li), which were not included in [2] due to difficulties in handling very soft materials. The authors of [2] did not produce satisfactory results for the alkaline earth metals regarding elastic constants and phonon spectra, and did not present Molecular Dynamics (MD) simulations for these metals. Also, TB calculations for alkali metals were not attempted in [2]. In this dissertation, robust TB parametrizations have been obtained for Sr, Ca and Rb; also limitations of the method for Li have been presented. In trying to complement and improve on the TB results of [2], two problems were identified: (i) The first-principles Linear Augmented Plane Wave (LAPW) calculations based on the Generalized Gradient Approximation (GGA) provide a more accurate input to the NRL-TB than the LAPW Local Density Approximation (LDA) used in [2], because it gives a better agreement with experiment for the equilibrium lattice parameter. (ii) In order to successfully perform MD simulations, the LAPW total energy inputs to the TB need to be extended to much smaller volumes than those considered in [2]. The central feature of this dissertation is about creating a good TB parametrization for the metals Sr, Ca, and Rb that accounts well for the band structure, and density of

states, as well as producing accurate total energies for the evaluation of structural differences, elastic constants, phonon frequencies and the MD derived quantities Mean Square Displacement (MSD) and Vacancy Formation Energy (VFE). Also, insights are presented for the application of the method to the very light element Li.

Chapter 1: Introduction

High performance computers are used increasingly to predict materials with new and better properties. Computational methods help in understanding electronic, thermal, magnetic, chemical, structural and optical properties. Models and simulations are increasingly used to predict nature and behavior of materials. The two major considerations in choosing such methods are speed and accuracy. By calculating total energy and band structure of materials, many predictions can be made regarding properties of a material. These include elastic constants which predict the mechanical stability of a material, Density of States (DOS), electronic specific heat coefficient, phase transition pressures and temperatures, phonon frequencies, and Molecular Dynamics (MD), and derived quantities like Mean Square Displacement (MSD) and Vacancy Formation Energy (VFE).

A method of modeling that has been successful in predicting such properties is the Naval Research Laboratory (NRL)-Tight-Binding (TB) method, which was introduced by Cohen, Mehl, and Papaconstantopoulos [1], and was applied successfully to an array of metallic and transition metallic elements in 1996 [2]. This method has also been extended to also cover magnetism [3, 4]. Further, it has been used to study phase transitions in high pressure [5], new superconductors like MgB_2 [6], and semiconductors like Si [7], Ge [8], and SiC [9].

There are several advantages of using the NRL-TB method: *(i)* There is significant improvement on speed, i.e, the computational time, when compared to first-principles calculations. This is because the NRL-TB method describes the atoms in terms of atomic orbitals, usually 9 for cubic elements or 18 for hexagonal close packed (hcp) and diamond structures. This reduces the matrix size used in the calculation by almost 10 times, hence, reducing overall computation time by a factor of 10^3 , when compared to

Group →	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
↓ Period																		
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn

Figure 1.1: The Periodic Table showing elements that have been successfully parametrized using the NRL-TB method (in green), and focus of this work, Alkaline earth metals: Ca and Sr, and Alkali metals: Rb and Li (in grey).

first-principles calculations. *(ii)* In spite of reduced computational time, the NRL-TB method does not compromise on accuracy of the physical properties predicted. It gives excellent agreement with experiment: for lattice constants with error of only $\pm 2\%$, for bulk modulus $\pm 5\%$, for elastic constants $\pm 10\%$, and for phonon frequencies $\pm 5\%$. *(iii)* This method provides transferable parameters which enable prediction of properties of structures not included in the fit. *(iv)* Data inputs to this method can be from either first-principles calculations or experiment, which makes this method easier to use, compared to other total energy tight binding models.

Fig. 1.1 shows the Periodic Table indicating in green, the elements for which this method has been successful. However, the Linear Augmented Plane Wave (LAPW) and Local Density Approximation (LDA), which were used to generate inputs to NRL-TB, which has mixed results for alkaline earth metals such as Strontium (Sr) and Calcium (Ca), like poor elastic constants, phonon spectra and MD simulations. Also, alkali metals such as Rubidium (Rb) and Lithium (Li) were not included in [2] due to difficulties in handling very soft materials. In this dissertation, the two main issues mentioned in [2] are addressed, regarding alkaline earth metals and alkali metals. Firstly, the LAPW LDA input to the NRL-TB did not give a good agreement with experiment for the equilibrium lattice parameter. In this work, this issue has been resolved by using inputs from the LAPW GGA method, which was introduced by Perdew and Wang [10]. Also, smaller

volumes were not considered in [2], and this inhibited successful MD simulations. In this work, good TB parametrization for the metals Sr, Ca, and Rb have been successfully generated, which overcome these problems as well as account for band structure, and DOS, as well as producing accurate total energies for the evaluation of structural differences, elastic constants, phonon frequencies and the MD, and derived quantities MSD and VFE. Also, since the NRL group has not given successful TB parametrizations for the alkali metals, partly due to their softness, and also due to the fact that Density Functional Theory (DFT) gives total energies for face centered cubic (fcc), body centered cubic (bcc), and hcp, which are extremely close to each other. Further, a good TB Hamiltonian for one alkali metal, i.e., Rb has been obtained, which has only one atom is the outermost orbit, and provides a challenge. Also presented are insights for the application of the method to the very light element Li.

This dissertation is composed of 7 Chapters. In Chapter 2, the computational approaches and methods are discussed. Chapters 3, 4, 5, and 6 elaborate on results obtained for alkaline earth metals: Sr, and Ca, and alkali metals: Rb, and Li respectively. Chapter 7 provides a summary and direction for proposed future work.

Chapter 3 presents for Sr, the total energies for the following structures: fcc, bcc, simple cubic (sc), hcp, and diamond; the elastic constants for both bcc and fcc structures at equilibrium conditions; the DOS, the electronic specific heat coefficient, the band structure for fcc, MD calculations for both fcc and bcc structures, MSD, VFE, enthalpy and the phonon spectrum for the fcc structure at equilibrium conditions. Also effects of pressure on phonon frequencies, elastic constants and phase change in Sr are demonstrated. The MD calculations also show evidence of phase change with change in temperature.

Similar results for Ca and Rb are reported in Chapters 4 and 5 respectively, and in addition, the need for two sets of TB parameters to describe these elements accurately are discussed, as well as using a repulsive potential in the MD simulation.

Chapter 6 gives an overview of applying the NRL-TB method to Li and related chal-

lenges.

In Chapter 7, the results of this work and provide direction for future work have been summarized.

Chapter 2: Approach and Methods

2.1 Introduction

In this chapter, a brief overview of the computational theory and techniques used to study electronic structure calculations have been presented. The first step in such calculations is solving the time independent Schrödinger equation, which are usually called first principles or *ab initio* calculations. These are computationally time consuming, since they make as few approximations as possible and complexity increases with number of atoms present in the system. Density Functional Theory (DFT) relates total energy of a system and the ground state electronic density. In 1964, Hohenberg and Kohn [11] have shown that the ground state electronic density is the density when the energy is minimum. This made it practical to represent the total energy of a system as a sum of energies and also reduced a many-body problem to a single-body problem [11] and [12]. In calculating the total energies using DFT, there is a term which relates to the many body interaction called exchange correlation energy. This is usually approximated using either Local Density Approximation (LDA) or Generalized Gradient Approximation (GGA).

All these methods can be used to predict various electronic and mechanical properties of solids. By calculating the total energy of a material of the stable structure, the equilibrium volume and the elastic constants are determined. Calculating the energy bands and the density of states leads to the evaluation of the Fermi surface.

The Naval Research Laboratory (NRL)-Tight-Binding (TB) method maps total energies and energy bands inputs from LDA or GGA to a set of transferable TB parameters. It reduces significantly the computational time by a factor of 10^3 , with respect to first principles calculations. These TB parameters can be used to predict total energies of other structures, elastic constants, phonon frequencies, Density of States (DOS), electronic

specific heat coefficient, etc. These TB parameters have been successfully generated for metallic and transition metallic elements [2].

2.2 Density Functional Theory

The band theory of solids mainly solves the Schrödinger equation in reciprocal lattice space defined in Eq. (2.1), and these calculations are called first principles or *ab initio* calculations:

$$H\psi = \epsilon_i\psi. \quad (2.1)$$

DFT introduced by Hohenberg and Kohn in [11] evaluates the total energy of a system based on a functional of the ground state electronic density ϱ . Also, the density that minimizes energy $E(\varrho)$ is the ground state density. DFT also helped to reduce a many-body problem to a one-body problem without losing numerical accuracy. The total energy of the system can be written as :

$$E(\varrho) = E_h(\varrho) + E_{xc}(\varrho), \quad (2.2)$$

where E_h is the Hartree energy, which can be defined as:

$$E_h(\varrho) = T(\varrho) + E_{e-e}(\varrho) + E_{e-n}(\varrho) + E_{n-n}(\varrho). \quad (2.3)$$

In Eq. (2.3), $T(\varrho)$ is the kinetic energy of a single particle, which is found from the sum of the eigenvalues defined in Eq. (2.1). $E_{e-e}(\varrho)$ is the Coulomb interaction between electrons, $E_{e-n}(\varrho)$ is interaction between electrons and nuclei, and $E_{n-n}(\varrho)$ is the nuclei interaction energy. The $E_{xc}(\varrho)$ in Eq. (2.2) is the exchange and correlation energy which is approximated, usually, using either LDA or GGA. For LDA, the $E_{xc}(\varrho)$ is given by:

$$E_{xc}(\varrho) = \int \varrho(r)\epsilon_{xc}(\varrho(r))d^3r, \quad (2.4)$$

where $\epsilon_{xc}(\rho(r))$ is an approximation of energy of a uniform electron gas. The minimization of the $E(\rho)$ leads to single particle Schrödinger equation as follows:

$$\left[-\frac{\hbar^2}{2m} \nabla_i^2 + V(r) \right] \psi_i(r) = E \psi_i(r). \quad (2.5)$$

The charge density $\rho(r)$ is the usual summation over occupied states. i.e., $\rho(r) = \sum_i^{occ} \psi_i^* \psi_i$. The solution of the Schrödinger equation is then coupled with Poisson's equation, which relates $\rho(r)$ to the Coulomb potential $V_c(r)$, given as:

$$e \nabla^2 (V_c(r)) = -8\pi \rho(r). \quad (2.6)$$

The potential $V(r)$ in Eq. (2.5) is given by:

$$V(r) = V_c(r) + V_{xc}(r), \quad (2.7)$$

where $V_{xc}(r)$ is the exchange and correlation potential, which is approximated usually either using LDA or GGA.

2.3 Local Density Approximation

Hedin-Lundqvist [13], Perdew-Wang [10] and Weigner [14], have different prescriptions of LDA. The results obtained from the various forms of LDA have very small differences in the resulting electronic spectrum. The first practical applications of the LDA were made by Slater [15] and updated by Schwarz [16]. This form of LDA is known as the X_α method. In the X_α method, an exchange and correlation potential is constructed, which has the form:

$$V_{xc}(r) = \alpha \left(\frac{3\rho(r)}{8\pi} \right)^{\frac{1}{3}} = \alpha U_{ex}(r). \quad (2.8)$$

The coefficient α varies between $\frac{2}{3}$ and 1 to match the Hartree-Fock total energy of the atom. The Hedin-Lundqvist [13] exchange and correlation potential $V_{xc}(r)$ is given by

the expression:

$$V_{xc}(r) = \alpha\beta(r_s)U_{ex}(r), \quad (2.9)$$

where $\alpha = \frac{2}{3}$ is the Kohn-Sham parameter, and $\beta(r_s)$ is the so called correlation enhancement factor, which is given by:

$$\beta(r_s) = 1 + B \ln \left(1 + \frac{1}{x} \right), \quad (2.10)$$

where $r_s = \left(\frac{3}{4\pi\varrho(r)} \right)^{\frac{1}{3}}$, $x = \frac{r_s}{21}$ and $B = 0.7734$. Wigner [14] has provided an alternative expression for $\beta(r_s)$ as:

$$\beta(r_s) = 1 + \frac{0.9604r_s(r_s + 5.85)}{(r_s + 7.8)^2}, \quad (2.11)$$

which in some cases, as in alkali metals, give better agreement with measured lattice constants.

2.4 Generalized Gradient Approximation

GGA introduced by Perdew [17] improves on LDA by using a dependence of exchange and correlation energy on the derivative of the electron density, as well as $\varrho(r)$. In the GGA exchange and correlation energy, the gradient is not only a function of the density $\varrho(r)$, but it also depends on the gradient $\nabla\varrho$ as well. The generic functional form is written as:

$$E_{XC}^{GGA}(\varrho(r)) = \int \varrho(r) \epsilon_{XC}^{GGA}(\varrho(r)) |\nabla\varrho(r)| dr, \quad (2.12)$$

where ϵ_{XC}^{GGA} is the exchange and correlation energy per particle, and $\varrho(r)$ is the electron density. This approximation significantly reduced the error in the calculation of the total energy of atoms, binding energies and vibration frequencies. Also, GGA improves properties of simple metals, 3d transition metals, and alkali metals when compared to

LDA, which works in general for transition metals and semiconductors.

Variations of GGA includes the Vanderbilt GGA pseudopotential [18], in which the pseudopotential itself becomes charge-state dependent. However, this approach works well only with transition metal systems. In this work, the Perdew-Wang [10] exchange correlation potential has been used, which works for alkaline earth and alkali metals.

2.5 Born-Oppenheimer Approximation

When solving Eq. (2.3) of band theory, the Born-Oppenheimer Approximation has been used, which assumes that the nuclei are at rest at the positions that they would occupy in the crystal at temperature $T = 0K$. This means that the Schrödinger equation given in Eq. (2.5) is only solved for the motion of electrons around the fixed “frozen” nuclei. Thus, electronic motion is separated from nucleic motion. This is justified due to the large difference in mass between electrons and nuclei.

2.6 Units in Band Theory

The usual choice for units in band theory is: atomic unit of length (a.u.) = Radius of the first Bohr orbit = $\hbar^2/me^2 = 0.529 \text{ \AA}$. Unit of energy = Ionization energy of a Hydrogen atom = $me^4/1\hbar^2 = 1 \text{ Rydberg (Ry)}$. 1 Ry is defined as 13.06058 eV. The other unit of energy commonly used is *Hartree*, which is equal to 2 Ry. Using these units simplify Eq. (2.5), as the factor $\frac{\hbar^2}{2m}$ reduces to unity, hence, the Schrödinger equation becomes:

$$[-\nabla_i^2 + V(r)]\psi_i(r) = E\psi(r) \quad (2.13)$$

Hence, when $\hbar = 1$, mass of electron $m_e = \frac{1}{2}$, and charge of electron $e = 1$. Use of these simplified units reduce numerical errors.

2.7 Electronic Structure Methods

The Schrödinger equation is solved by an expansion of the wave-function:

$$\psi(r) = \sum_j a_j \phi_j(r). \quad (2.14)$$

This expansion converts the Schrödinger equation into a system of linear algebraic equations. The form of ϕ is what distinguishes one method from another, as well as how the core electrons are described. If the method accounts for all electrons in the system, then they are known as all-electron methods. An example of this is the Augmented Plane Wave (APW) method, which defines ϕ with spherical harmonics inside a muffin-tin sphere surrounding the atomic sites. The interstitial region, outside the spheres, is defined by plane waves. The Muffin-Tin Orbitals (MTO) method uses Bessel functions to describe wavefunctions inside the spheres and Neumann functions for the interstitial regions. The linearization procedure proposed by Andersen [19] has significantly improved the efficiency of the APW and MTO methods, leading to the Linear Augmented Plane Wave (LAPW) and the Linear Muffin-Tin Orbitals (LMTO) methods respectively. In this project, LAPW has been used with some minor changes and GGA integrated into it, henceforth, referred to as LAPW-GGA.

Another class of methods freezes the core electrons separating them from the valence electrons. These are known as pseudopotential methods, and these use plane waves to describe the wavefunction. The Vienna Ab-Initio Simulation Package (VASP) is a well-known, and commercially available package, which uses the pseudopotential method [20].

2.8 Augmented Plane Wave Method

The APW method, originally proposed by Slater [21] solves the DFT equations by approximating the energy states of electrons. This method of approximation is called the Muffin-Tin Approximation (MTA), and is generally used for cubic structures. It

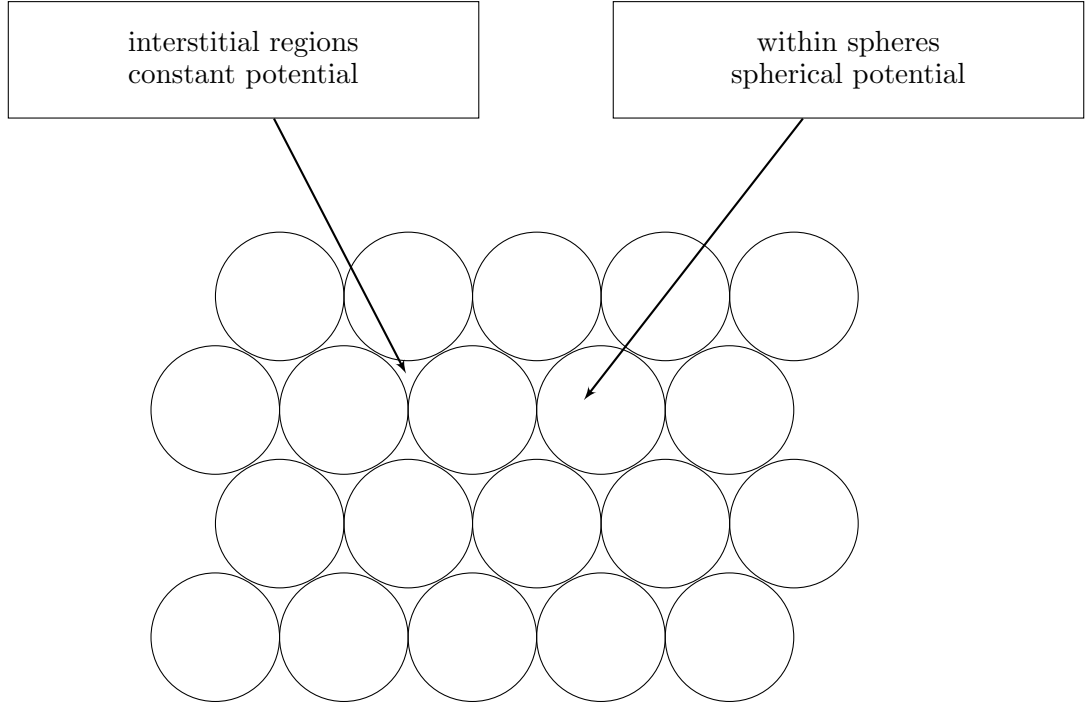


Figure 2.1: Muffin-tin spheres.

assumes that the energy is spherically symmetrical within spheres centred at every atom, and the energy at interstitial regions is considered to be constant. In MTA, each atomic site is surrounded by a sphere. Inside the sphere, the potential $V(r)$ is a spherical function of $V(|\mathbf{r} - \mathbf{R}_n|)$, and in the interstitial region, the potential is assumed to be constant V_c . This is illustrated in Fig. 2.1. Outside the muffin-tin spheres, i.e., in the interstitial region, MTA has a form of a plane wave, and is given by:

$$\phi(r) = \exp(ik \cdot \mathbf{r}). \quad (2.15)$$

Inside the sphere, the atomic wavefunction is found by solving the free-atom Schrödinger equation in spherical harmonics Y_{lm} , and is given by:

$$\phi(r) = \sum_{lm} A_{lm} Y_{lm}(r) u_l(r, \epsilon), \quad (2.16)$$

where A_{lm} is determined by the boundary conditions to maintain continuity, and u_l is calculated by solving the radial equation at each k-point in the Brillouin zone, given by:

$$-\frac{1}{2r^2} \frac{d}{dr} \left(r^2 \frac{du_l(r)}{dr} \right) + \left[\frac{l(l+1)}{r^2} + V(r) - \epsilon_l \right] u_l(r) = 0, \quad (2.17)$$

where $V(r)$ is a periodic function which is obtained by solving Poisson's equation using a self-consistent procedure. Since the potential $V(r)$ is periodic, the wave function satisfies the Bloch condition:

$$\Psi(r + G_n, k) = e^{ikG_n} \Psi(r, k). \quad (2.18)$$

Substituting Eq. (2.14) into Eq. (2.1), a system of N algebraic equations is obtained:

$$\sum_{j=1}^N (H - \epsilon)_{ij} C_{kj} = 0. \quad (2.19)$$

The APW matrix elements include Legendre polynomials, spherical Bessel functions and logarithmic derivatives in Eq. (2.17), which are evaluated at the MTA radius R_s . Once the matrix elements are calculated, an eigenvalue problem is solved by diagonalizing the matrix.

2.9 Linearized Augmented Plane Wave Method

We have used LAPW, which is described by Andersen [19] combined with GGA to calculate total energies of cubic structures. The LAPW method improves on the APW method by matching the basis functions and their derivatives to a radial wavefunction at ϵ_l . This is known as linearization of the APW functions, which solve problems in the diagonalization of the APW secular equations and facilitates the implementation of a general potential, i.e., the LAPW codes remove the MT approximation by using a general potential, which is not constant outside the MT spheres and non-spherically symmetric inside.

Calculations are performed on body centered cubic (bcc), face centered cubic (fcc) and simple cubic (sc) using 55, 85 and 35 uniform k-points respectively. The LAPW method is combined with the Perdew-Wang [10] method of the GGA, and henceforth refer to it as LAPW-GGA.

2.10 Scalar Relativistic Approach

Relativistic effects cannot be ignored for heavier elements and hence, a relativistic Hamiltonian is used, which is described as:

$$H = H_{NR} - \frac{p^4}{8m^3c^2} + \frac{\hbar^2}{8m^2c^2} \nabla^2 V + \frac{\hbar^2}{4m^2c^2 r} \frac{dV}{dr} (\rho.L), \quad (2.20)$$

where the H_{NR} is the non-relativistic Hamiltonian, and the 2nd term in the right hand side, is the mass-velocity term, representing the relativistic correction to the kinetic energy $\frac{p^2}{2m}$. It is usually negative and larger for s-like states. The 3rd term represents the correction of centrifugal potential, which is called a Darwin term, and affects only s-like wavefunctions. The 4th term represents spin-orbit coupling, and is significant for semiconductors like Ge and 5d elements and higher. Including this 4th term is called the Fully Relativistic Approach. In this study, only the first 3 terms are used, and the spin-orbit term is omitted, which is called the Scalar Relativistic Approach.

2.11 Self Consistent Cycle

The self consistent cycle consists of the following major steps:

1. Making an initial guess of charge density from superposition of atomic charge densities.
2. Solving scalar-relativistic Schrödinger equation to compute new charge density as well as Schrödinger equation for the atomic-like core states.
3. Solving Poisson equation to get a new potential.

4. Mixing old and new charge density, and applying to the SE to repeat the process.

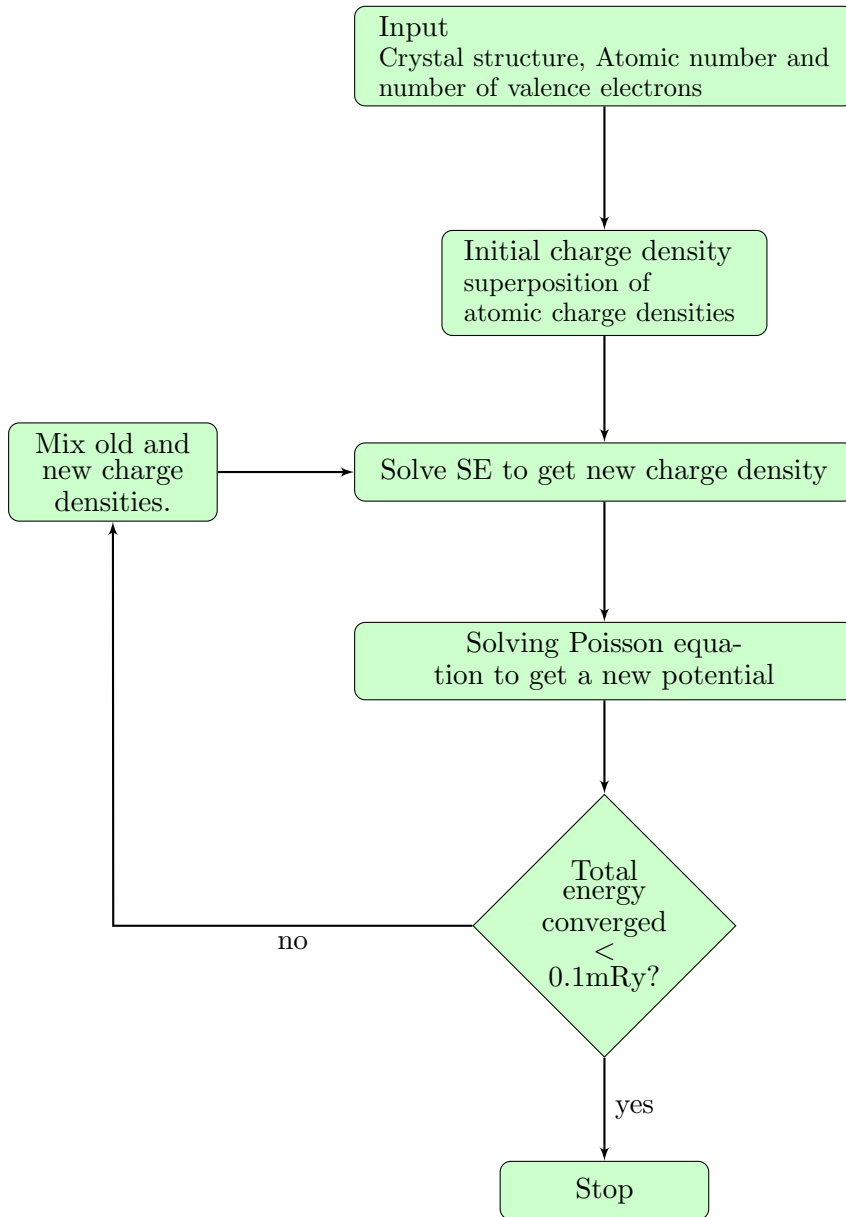


Figure 2.2: Self consistent cycle.

The above steps, shown in Fig. 2.2 must be repeated until the electron density has converged to the tolerance value or the total energy has reached a convergence of about 0.1 mRy.

2.12 Total Energy

The DFT calculations using APW or LAPW give total energy $E(V)$ as a function of volume (lattice constant). By examining the relationship between lattice constant and total energy, the equilibrium lattice constant is determined as that with the minimum energy. Birch [22] fit is used to determine this minimum energy using the relation:

$$E(v) = \sum_i^N a_i V^{-\frac{2i}{3}}, \quad (2.21)$$

where a_i are the expansion coefficients and N is the order of fit. Usually, N is chosen to be 3, since the total energy tends to vary in a parabolic fashion. With $N = 3$, Eq. (2.21) transforms to:

$$E(V) = E_0 + \frac{9V_0 B_0}{16} \left\{ \left[\left(\frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right]^3 B'_0 + \left[\left(\frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right]^2 \left[6 - 4 \left(\frac{V_0}{V} \right)^{\frac{2}{3}} \right] \right\}, \quad (2.22)$$

where V_0 is the equilibrium volume, V is the deformed volume, B_0 is the equilibrium bulk modulus, and B'_0 is the derivative of the bulk modulus with respect to pressure. The bulk modulus is calculated from the second derivative of the total energy with respect to volume as:

$$B_0 = -V \left(\frac{\partial P}{\partial V} \right)_{P=0} = -V \frac{d^2 E}{dV^2}. \quad (2.23)$$

Hence, Birch fit determines the equilibrium lattice constant as well as the bulk modulus.

2.13 Tight-Binding

Various schemes of TB exist, originating from writing the wave function as a Linear Combination of Atomic Orbitals (LCAO). The resulting integrals are used as adjustable parameters, which maps results of first principles calculations to a Slater-Koster (SK) basis set as originally proposed by Slater and Koster [23]. The NRL-TB method de-

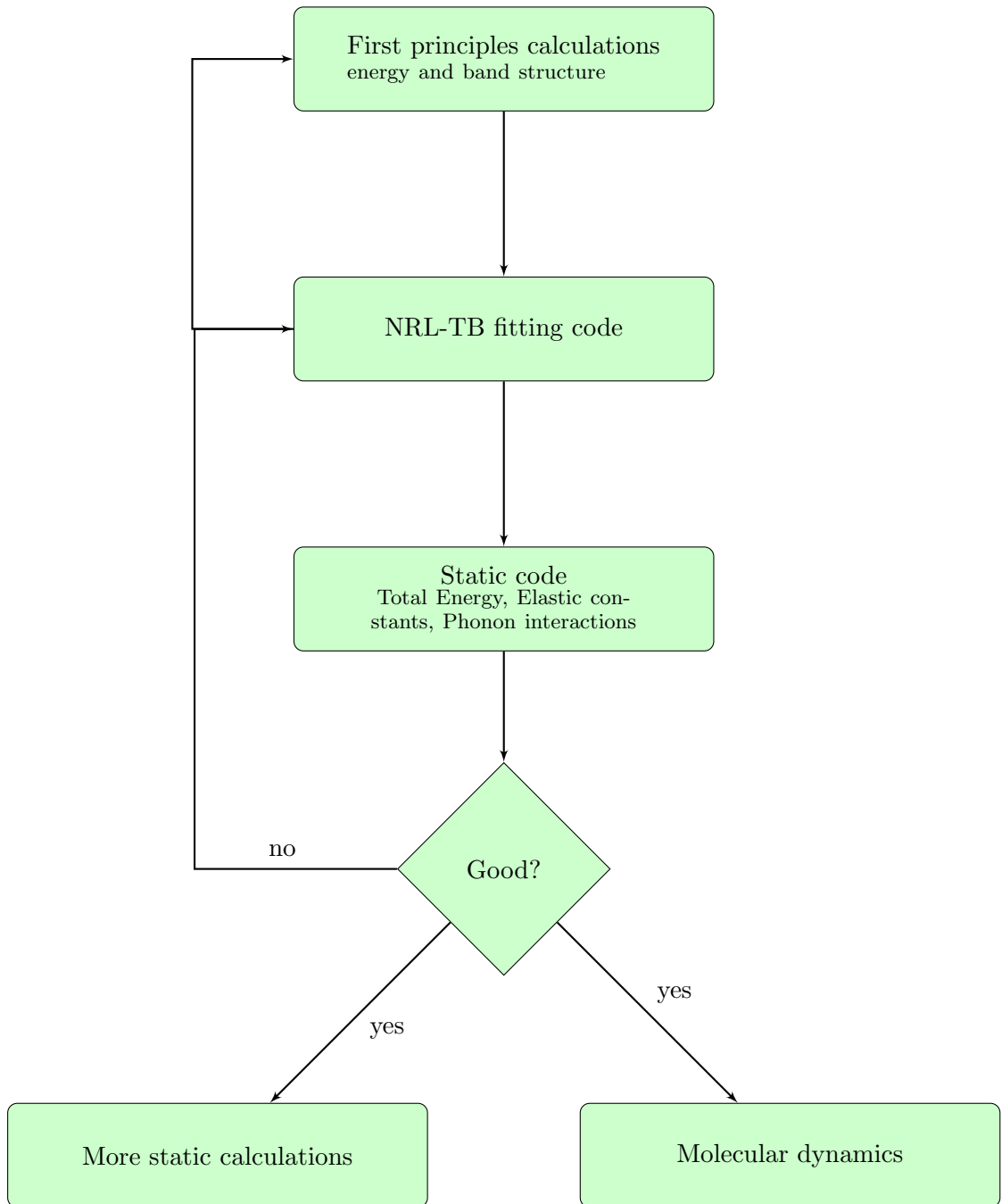


Figure 2.3: NRL-TB method of electronic structure calculations.

scribes the atoms in terms of atomic orbitals, s , p and d , 9 for monoatomic, 18 for diatomic, etc. This reduces the matrix size used in the calculation by almost 10 times, hence reducing overall computation time by a factor of 10^3 , when compared to more

accurate first-principles calculations. This process is illustrated in Fig. 2.3. A non-orthogonal two-center SK form is used, which calculates three types of parameters: on-site, Hamiltonian, and overlap. The non-orthogonal TB model is represented as:

$$H_{m,n}(k) - ES_{m,n}(k) = 0, \quad (2.24)$$

where H is the Hamiltonian and S is the overlap matrix. On-site parameters represent energy of an electron in an orbital, Hamiltonian parameters represent the matrix elements for electron to hop from one site to another, and are defined as:

$$H_{nm} = \sum_{\mathbf{R}_j} \exp[i\mathbf{k} \cdot \mathbf{R}_{ij}] \int \phi_n^*(\mathbf{r} - \mathbf{R}_i) \tilde{H} \phi_m(\mathbf{r} - \mathbf{R}_j) d^3r, \quad (2.25)$$

where $\mathbf{R}_{ij} = \mathbf{R}_i - \mathbf{R}_j$ depends on positions of atoms i and j . Overlap matrix elements represent the mixing between non-orthogonal orbitals and their neighbors, and are defined as:

$$S_{nm} = \sum_{\mathbf{R}_j} \exp[i\mathbf{k} \cdot (\mathbf{R}_{ij})] \int \phi_n^*(\mathbf{r} - \mathbf{R}_i) \phi_m(\mathbf{r} - \mathbf{R}_j) d^3r, \quad (2.26)$$

where H and S are integrals based on the positions of atoms on orbitals ϕ_n and ϕ_m . The integrals can be evaluated directly, however, these integrals are replaced with parameters that are determined from first-principles results, usually at points and directions of high symmetry in the Brillouin zone for different structures and volumes. Size of H and S depends on the number of atoms in a unit cell, and the number of atomic orbitals on each site, i.e., 1s, 3p and 5d, which give a 9 x 9 matrix. The diagonal elements of the parametrized H matrix are calculated as:

$$h_{i\alpha} = a_{i\alpha} + b_{i\alpha} \rho_i^{2/3} + c_{i\alpha} \rho_i^{4/3} + d_{i\alpha} \rho_i^2, \quad (2.27)$$

where α is the angular momentum and can be either s, p or d , and ρ is the atomic density. d can be further split into t_{2g} and e_g , and ρ is defined as:

$$\rho = \sum \exp \left[-\lambda_{ij} R_{ij} \right] F_c(R_{ij}), \quad (2.28)$$

where F_c is a cutoff function, which depends on cutoff radius R_0 , and is given as:

$$F_c(R) = \left(1 + \exp(R - R_0) \right)^{-1}. \quad (2.29)$$

For calculations in this study, $R_0 = 16.5a_0$, and $l = 0.5a_0$, where a_0 is the Bohr radius. Hence, $a, b, c, 2d$ and λ altogether contribute 17 parameters. Hopping coefficients define the energy required for an electron to hop from one site to another. It is represented as a 2nd order polynomial, given by:

$$H_{ll'm}(r) = (e_{ll'm} + f_{ll'm}r + g_{ll'm}r^2) \exp(-h_{ll'm}^2 r) F(r), \quad (2.30)$$

where $ll'm$ can be $ss\sigma, sp\sigma, pp\sigma, pp\pi, sd\sigma, pd\sigma, pd\pi, dd\sigma, dd\pi$, and $dd\delta$, and $F(r)$ is the cutoff function given as in Eq. (2.29). This generates 40 coefficients, which are to be determined by a least squares fit to the first principles results. Similarly, overlap coefficients define the energy describing mixing between non-orthogonal orbitals on neighbour sites, which are also represented as a 2nd order polynomial similar to Eq. (2.30):

$$S_{ll'm}(r) = (p_{ll'm} + q_{ll'm}r + r_{ll'm}r^2) \exp(-s_{ll'm}^2 r) F(r), \quad (2.31)$$

where $p_{ll'm}, q_{ll'm}, r_{ll'm}$, and $s_{ll'm}$ are the corresponding parameters of the overlap matrix.. Eq. (2.31) also generates 40 coefficients, and hence, a total of 97 coefficients are generated from the least squares fit.

Most TB approaches define total energy as a sum of a band energy term and a repulsive potential $G[\rho(r)]$, that is equivalent to replacing all the charge density $\rho(r)$ dependent

terms appearing in the total energy expression of the DFT. In the NRL-TB method, G is eliminated by defining a quantity V_o as:

$$V_o = \frac{G[\rho(r)]}{N_e}, \quad (2.32)$$

where N_e is the number of valence electrons. Then, all the first-principles eigenvalues $\epsilon_i(k)$ are shifted by the constant V_o and a shifted eigenvalue is defined as:

$$\epsilon'_i(k) = \epsilon_i(k) + V_o. \quad (2.33)$$

This results in the first-principles total energy E as:

$$E = \sum \epsilon'_i(k), \quad (2.34)$$

where the sum is over all occupied bands and all k-points in the Brillouin zone. V_o is different for each volume and structure of the first principles database. This shift does not affect the exact shape of the first-principles bands. Once this shift is complete, a least squares procedure is used to fit this database with the shifted eigenvalues ϵ'_i to the NRL-TB Hamiltonian.

NRL-TB method minimizes the total energy and eigenvalue differences between the TB and first-principles calculations using the Levenberg-Marquardt Algorithm (LMA) [24], also known as the Damped Least Squares (DLS) method as shown:

$$M = \sum_i^j \omega_E(i) |E_{LAPW}(i) - E_{TB}(i)|^2 + \sum_{i,k,n} \omega_B(i, k, n) |\varepsilon_{LAPW}(i, k, n) - \varepsilon_{TB}(i, k, n)|^2. \quad (2.35)$$

where ω_E is a weighting factor for the total energy value for structure i , ω_B is the weighting factor for eigenvalue of the k^{th} k-point and band n for structure i .

This method has been extended to also cover magnetism in [3] and [4]. Also, it has

been used to study phase transitions in high pressure [5], new superconductors like MgB_2 [6], and semiconductors like SiC [9].

2.14 Elastic Constants

Here, the equations associated with computing elastic constants of a system with cubic symmetry are discussed. Elastic constants C_{ij} determine mechanical stability of a material by determining reaction of the material to external forces, and they measure the relationship between strain and stress in a crystal, provided that the strain is not so large as to violate Hook's law [25]. They can be determined by applying a strain to a crystal, measuring energy v. strain and then determining the elastic constant from the curvature of this function at zero strain [26]. A given strain is associated with a certain linear combination of elastic constants.

For a given strain matrix e_i , the total energy changes by an amount given by:

$$E(e_i) = E_0 - P(V)\Delta V + V \sum_{i=1}^6 \sum_{j=1}^6 \frac{1}{2} C_{ij} e_i e_j + O(e_i^3), \quad (2.36)$$

where V is the volume of the undistorted lattice, $P(V)$ is the pressure of the undistorted lattice at volume V , ΔV is the change in the volume of the lattice due to the strain and $O(e_i^3)$ indicates the neglected terms in the polynomial expansion, which are cubic and higher powers of e_i . There are 21 independent elastic constants C_{ij} in Eq. (2.36). Due to symmetry of cubic materials, including diamond, these reduce to 3. For cubic lattices, the bulk modulus B given in Eq. (2.37) of a system is also significant in determining mechanical stability and is related to the elastic constants by:

$$B = \frac{1}{3}(C_{11} + 2C_{12}). \quad (2.37)$$

The other two constants selected to complete the set for cubic lattices are shear moduli $C_{11} - C_{12}$ and C_{44} . These are important for mechanical stability and need to satisfy the

following conditions at the equilibrium of the equation of state:

$$B = \frac{1}{3}(C_{11} + 2C_{12}) > 0,$$

$$C_{11} - C_{12} > 0, \quad \text{and} \quad C_{44} > 0.$$

Initially, $C_{11} - C_{12}$ was calculated using tetragonal strain [27], and now a volume conserving orthorhombic strain is used, which is given by:

$$e_1 = -e_2 = x,$$

$$e_3 = \frac{x^2}{(1 - x^2)}, \quad \text{and}$$

$$e_4 = e_5 = e_6 = 0.$$

This allows the energy to be an even function of orthorhombic strain x and is determined as:

$$\Delta E(x) = \Delta E(-x) = V(C_{11} - C_{12})x^2 + O(x^4). \quad (2.38)$$

Compared to tetragonal symmetry method, this needs only half the number of computations, even though more independent k-points are required in the Brillouin zone. $C_{11} - C_{12}$ can be determined from the slope of Eq. (2.38). Similarly, for C_{44} , a volume conserving monoclinic strain is used, which is given by:

$$e_6 = x,$$

$$e_3 = \frac{x^2}{(4 - x^2)}, \quad \text{and}$$

$$e_1 = e_2 = e_4 = e_5 = 0,$$

Again, the elastic constant C_{44} is determined from the slope of the following equation:

$$\Delta E(x) = \Delta E(-x) = \frac{1}{2}VC_{44}x^2 + O(x^4). \quad (2.39)$$

Here, x is the monoclinic strain, and E is the energy of the system under such a strain. More detailed calculations, including tetragonal $L1_0$ lattice, have been explained in [26]. Calculations for fcc $C_{11} - C_{12}$ and C_{44} have 1688 and 1590 k-points respectively, and bcc elastic constants have 189 and 185 k-points respectively.

2.15 Density of States

The density of states (DOS) is defined as the number of states per unit energy. To calculate DOS, first principles results in k-space are interpolated. The tetrahedron method [28] is an efficient way to calculate DOS, in which eigenvalues are interpolated linearly according to the formula:

$$\epsilon(\vec{k}) = \epsilon_0(k) + \vec{b} \cdot (\vec{k} - \vec{k}_0), \quad (2.40)$$

where ϵ_0 and $\vec{b}$ are determined by the energies at the corners of the tetrahedron. DOS calculated in this method, denoted by $N(E_f)$, where E_f is the Fermi energy, can be verified with different spectroscopic measurements.

The electronic specific heat coefficient γ is related to $N(E_f)$ as:

$$\gamma = 0.1734(1 + \lambda)N(E_f), \quad (2.41)$$

where $N(E_f)$ is expressed in *states/Ry/atom* and γ is given in *mJ/(mol deg²)*. For calculations in this study, mass enhancement factor $(1 + \lambda)$ has been ignored, and hence, γ should be smaller than experiment.

2.16 Tight-Binding Molecular Dynamics

All calculations so far are limited to ambient temperature of $T = 0K$. To study properties at finite temperatures, Molecular Dynamics (MD) has been used, which allows a system of atoms to move in time. By examining the averages of the physical properties in time, a perspective on how the material will behave under change in temperature

can be examined. The parameters generated using the NRL-TB method are used with the Tight-Binding Molecular Dynamics (TBMD) package by Kirchhoff et al. [29] to determine thermodynamic properties such as melting temperatures, phase transformation of a crystal with change in temperature, and the atomic Mean Square Displacement (MSD), and Vacancy Formation Energy (VFE).

Initially, for a temperature of $2T$, atoms are arranged on a lattice with initial velocities assigned randomly from a Boltzmann distribution. A microcanonical ensemble or NVE ensemble, in which number of atoms (N), volume (V) and energy (E) are all conserved, is used in the MD simulation. In this ensemble, the potential energy and kinetic energy are exchanged to conserve energy until the temperature of the lattice averaged to T at equilibrium. According to the kinetic theory of gases, temperature is nothing but the average kinetic energy of the system given by $dk_B T/2$, where d is the system dimension (3 in this case), and k_B is Boltzmann's constant. The atomic kinetic energy at any time step is $\frac{1}{2}mv^2$, which can be easily averaged for all atoms, and thus, instantaneous temperature can be calculated. If this calculated temperature is not the desired target temperature T , the velocities of each atom are scaled, and the process is repeated. This is called equilibration, and it is performed for 2000 time steps. Verlet algorithm [30] has been used to integrate the equations of motion at time step of $\Delta t = 2$ fs.

In addition, a hard core repulsion is used for TBMD which is specified by Bernstein [31], for Calcium (Ca) and Rubidium (Rb). It specifies, in Bohr, the inner cutoff distance r_i and outer cutoff distance r_o for pair repulsion. For distances greater than r_o , the energy contribution is exactly zero. The energy goes to $+\infty$ at an interatomic distance of r_i . This modifies the total energy to:

$$E_{tot} = E_{elec} + E_{rep}, \quad (2.42)$$

where

$$E_{rep} = \sum_{\langle ij \rangle} V(r_{ij}). \quad (2.43)$$

$V(r_{ij})$ is of the form:

$$V(r) = \exp\left(\frac{r_o - r_i}{r - r_i} + \frac{r_o - r_i}{r - r_o}\right). \quad (2.44)$$

This form ensures that at $r \rightarrow r_i$, the argument of the exponential goes to $+\infty$, and so does V . At $r \rightarrow r_o$, the argument of the exponential goes to $-\infty$, and $V \rightarrow 0$.

Although, the code has both serial and parallel versions, the parallel version is used in this study, which uses a Message Passing Interface (MPI) model. TBMD has been performed for fcc and bcc structures, and a super-cell was used, which consisted of 343 atoms by replicated a single cell 7 times along the primitive lattice vectors. The simulation was performed for a total of 2000 steps for temperature ranging from 100 to 1000 K for Strontium (Sr), to 1300K for Ca, and to 400K for Rb

2.17 Mean Square Displacement

We have used the atomic positions generated by the TBMD simulations performed for several temperatures at the corresponding experimental lattice constants to compute the atomic MSD, which is an indication of atomic diffusivity, i.e., distance travelled by a particle over a time interval. It is an average of atomic positions, which are generated by TBMD over all atoms and time steps.

2.18 Vacancy Formation Energy

The VFE is calculated using the super-cell method, in which one atom is removed and the neighboring atoms are allowed to relax [32]. A large lattice of atoms is created and the center atom is removed, allowing the remaining atoms to relax or are fixed at their locations. VFE calculated from unrelaxed lattice is usually higher than that from a relaxed lattice. The potential energy of the system is then calculated with the experimental lattice constant without the defect. The VFE is defined as:

$$E_{vf} = E(N - 1, 1) - \left(\frac{N - 1}{N}\right) E(N, 0), \quad (2.45)$$

where $E(N, M)$ is the energy of the lattice containing N atoms and M vacancies. For calculations in this study, a $7 \times 7 \times 7$ matrix has been considered, which contributes $N = 343$ atoms. First $N = 343$ atoms and $M = 0$ vacancies are considered, and next calculation is for $N = 342$ atoms and $M = 1$ vacancy. Energy E_{vf} should be proportional to the number of atoms remaining in the system. A positive E_{vf} indicates that the crystal is more stable as a complete crystal without a vacancy. In this study, relaxed lattice has been achieved using the conjugate gradient method.

2.19 Enthalpy

Enthalpy represents total energy of a system and is given by:

$$H(P) = E + PV, \quad (2.46)$$

where H is the enthalpy, E is the energy, P is the pressure at volume V . Similar to predicting stable structure by looking at relationship between lattice constant and energy, the pressure graph can be examined for various lattices and determine phase changes under pressure. Pressure is calculated by the numerical differentiation of the total energy with respect to volume. The enthalpy of both fcc and bcc structures are calculated, and an intersection was found to determine the pressure at which phase change occurs.

2.20 Phonon Frequencies

A phonon describes vibrational mode, in which a lattice of atoms or molecules uniformly oscillates at a single frequency. The NRL-TB method is used to calculate phonon frequencies as a function of wave-vectors using the frozen phonon approximation method [33]. In this method, a super-cell similar to the one used for the vacancy formation calculations is computed, and atoms are displaced in a specified polarization direction [34]. First the total energy as a function of the amplitude of a “frozen” phonon wave in a solid is calculated, and then the curvature of the energy as a function of the wave amplitude

is calculated, and finally the normal mode frequency from the curvature is determined. The phonon frequency is determined by the value of the first derivative of the energy with respect to the displacement of the atoms from their equilibrium lattice positions. In the harmonic approximation [33], change in energy due to this displacement is given as:

$$U_{harmonic} = \frac{1}{2} \sum_{R, R', \alpha, \beta} u^\alpha(R) \cdot D^{\alpha\beta}(R - R') \cdot u^\beta(R'), \quad (2.47)$$

where $u^\alpha(R)$ is the displacement from equilibrium of an atom α in a unit cell associated with lattice vector R , and $D^{\alpha\beta}(R - R')$ is the force constant matrix connecting atom α in unit cell R and atom β in unit cell R' . In the super-cell approximation, phonon frequencies can only be determined at those wave vectors which lead to reasonably sized super-cells of the primitive lattice. Thus, procedures to calculate the phonons on an 85 point mesh for fcc alkaline earth metals and 55 point mesh for the bcc alkali metals have been derived. Phonon frequency are calculated at X, L, W, Δ and Σ k-points in various traverse and longitudinal polarizations. For bcc alkali metals phonon frequency are calculated at Δ, H, N and P k-points in various traverse and longitudinal polarizations.

Chapter 3: Alkaline Earth Metal: Strontium

3.1 Strontium

Strontium (Sr) is an alkaline earth metal, which has been studied very intricately both experimentally and theoretically. Crystal structure of Sr is a function of temperature and pressure. The Naval Research Laboratory (NRL)-Tight-Binding (TB) method using Local Density Approximation (LDA), which was applied to transition and noble metals by Mehl et al. [2], also included alkaline earth metal Sr. However, elastic constants predicted, were not in good agreement with experiment for alkaline earth metals like Sr and Calcium (Ca), especially Sr's C_{44} had negative values. This inhibited further study of properties using other methods such as molecular dynamics, and hence, the calculations have been revisited in this work using TB calculations with Linear Augmented Plane Wave (LAPW)-Generalized Gradient Approximation (GGA) results as input.

Jayaraman et al. [35] have observed phase changes of Sr under high pressure. Embedded Atom Method (EAM) potential calculations presented by Sheng et al. [36] for 14 fcc metals include Sr and are in good agreement with results in this study. However, several other calculations using WEIN95 [37] and Full Potential (FP)-LAPW [38], both using LDA, incorrectly predict body centered cubic (bcc) as a ground state, in spite of correctly predicting other electronic properties. However, many other calculations correctly predict the ground state of Sr as face centered cubic (fcc), as in study of strained monoatomic cubic crystals [39] and assessment of alkaline earth metals under pressure [40].

At room temperature and normal pressure, the stable lattice structure of Sr is fcc; however, calculations by Skriver [41], using LDA has indicated that Sr transitions to bcc at 4.0 GPa. Experimentally, this transition has been verified by Olijnyk and Holzapfel [42]

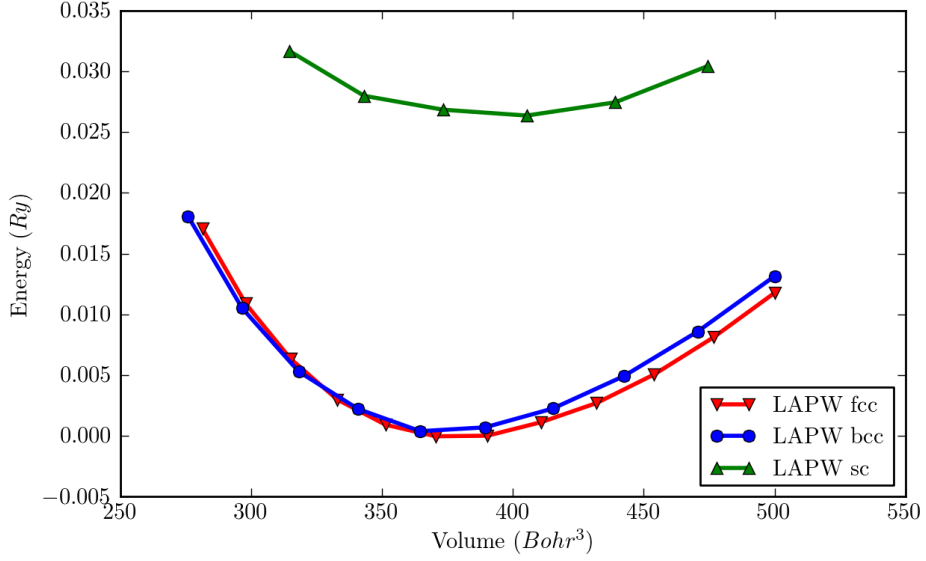


Figure 3.1: Total energies of Strontium fcc, bcc, and sc lattices generated using LAPW-GGA.

to be 3.5 GPa and Skriver again verified it to be 3.8 GPa [43]. Also, Jayaraman et al. [35] have predicted that Sr undergoes a phase change from fcc to bcc at a temperature of 830K. Sr is considered a semi-metal, since it transitions from metal to non-metal at lower pressures, hence, losing its metallic characteristics in the process as explained by Wang et al. [44].

Sr is much softer in nature than transition and noble metals, and hence, mechanical properties like elastic constants are very difficult to calculate. Sr has only s-like conduction electrons and an empty d-band above the Fermi level.

This chapter describes the results of LAPW-GGA calculations of several lattice structures of Sr as a function of pressure. The GGA results are in better agreement with experiment than the LDA. These results are input to the NRL-TB fit, which is the main objective of this work. The resulting TB Hamiltonian is then used to predict total energies that are input to the NRL-TB fit, which gives a set of 97 parameters. These parameters are then used to predict total energies for the following lattice structures: bcc, fcc, simple cubic (sc), hexagonal close packed (hcp), and diamond. Using the afore-

mentioned parameters, predictions have been made on mechanical properties like elastic constants, for both bcc and fcc structures, band structure, Density of States (DOS), phonon frequencies, enthalpy, Molecular Dynamics (MD), Mean Square Displacement (MSD), and Vacancy Formation Energy (VFE).

3.2 LAPW-GGA

Table 3.1: Comparisons of Strontium’s lattice constant and bulk modulus with experiment and other computational results.

	Lattice Constant (<i>Bohr</i>)	Bulk Modulus (<i>GPa</i>)
Present work LAPW-GGA input	11.490	14.55
Reference Handbook ^a	11.497	12.00
TB using LDA ^b	10.828	15.00
EAM potential ^c	11.476	11.00
Pseudopotential using VASP ^d LDA	10.904	15.00
Pseudopotential using VASP ^e GGA	11.282	12.00
FP LAPW ^f	10.902	16.50
FP LAPW ^g	11.437	11.00
PAW using VASP ^h	11.357	11.70

^aReference [45]

^bReference [2]

^cReference [36]

^dReference [46]

^eReference [46]

^fReference [38]

^gReference [40]

^hReference [47]

Using the LAPW-GGA program, total energies for fcc, bcc and sc structures have been calculated, since it provides better agreement with experiment for the lattice constant than LAPW-LDA. The LAPW-GGA has generated *ab initio* values for fcc in the range 10.60 – 12.20 Bohr, for bcc 8.20 – 10.00 Bohr, and for sc in the range of 7.00 – 7.80 Bohr. The equilibrium structure predicted is fcc and the lattice constant is 11.49 Bohr, which is 0.06% smaller than the experiment values as shown in Table 3.1. This is an improvement over the LDA results presented by Mehl et al. [2], and also are in good

agreement with other EAM potential calculations presented by Sheng et al. [36]. Certain calculations incorrectly predict bcc as a ground state, with energy difference as low as 0.05 mRy, such as WEIN95 [37] and FP LAPW [38], both using LDA. However, many other calculations correctly predict the ground state as fcc as in study of strained monoatomic cubic crystals [39], and study of alkaline earth metals under pressure [40].

By examining the 2nd derivative of the change in energy as the volume changes, the bulk modulus is calculated as 14.55 GPa. One experiment value for the bulk modulus of Sr at 0K is 12.00 GPa, which has been measured by Mizuki [48], however, Anderson [49] has measured it with more precision at 12.35 GPa. Other calculations using methods like EAM potential [36] and pseudopotential [50] calculated bulk modulus to be 12.00 GPa.

3.3 Tight-Binding

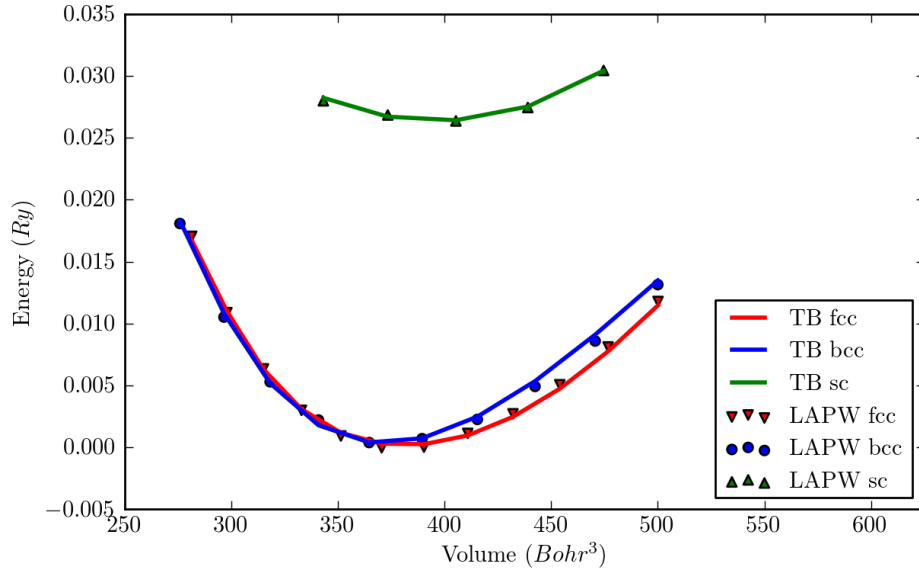


Figure 3.2: Total energies of Strontium's fcc and bcc lattices obtained from NRL-TB in comparison with input values from LAPW-GGA.

Non-orthogonal parameters, as listed in Appendix A.1, are generated to accommodate

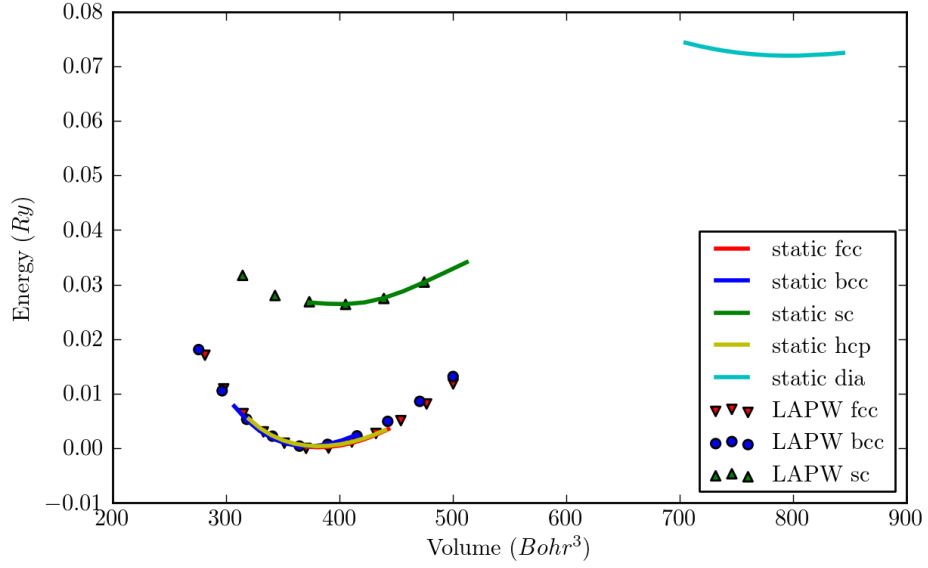


Figure 3.3: Total energies of fcc, bcc, sc, hcp, and dia structures for Strontium generated using the NRL-TB parameters compared with input values of fcc, bcc, and sc generated using LAPW-GGA.

more lattice constants for fcc and bcc. The range for fcc is 10.40 – 12.40 Bohr and for bcc, it is 8.20 – 10.00 Bohr. The fit generated a good agreement with the LAPW-GGA values as shown in Fig. 3.2. The total RMS error for the total energies is 0.000248 Ry showing an excellent TB fit, and that of the energy bands averages around 0.006 Ry. The band errors are a little higher than desired, but the TB parameters do produce reasonable results in predicting other electronic and mechanical properties which are not fitted.

As expected, fcc has the lowest total energy, and hence, in agreement with experiment that it is the stable lattice structure. The lattice constant corresponding to the lowest energy is 11.50 Bohr having a 0.02% change from the experiment values of 11.497 Bohr. The lowest lattice constant used in the fit for fcc is 10.60 Bohr, which is approximately 92% of the equilibrium lattice constant and hence, the parameters may be used as an input to the Tight-Binding Molecular Dynamics (TBMD) program.

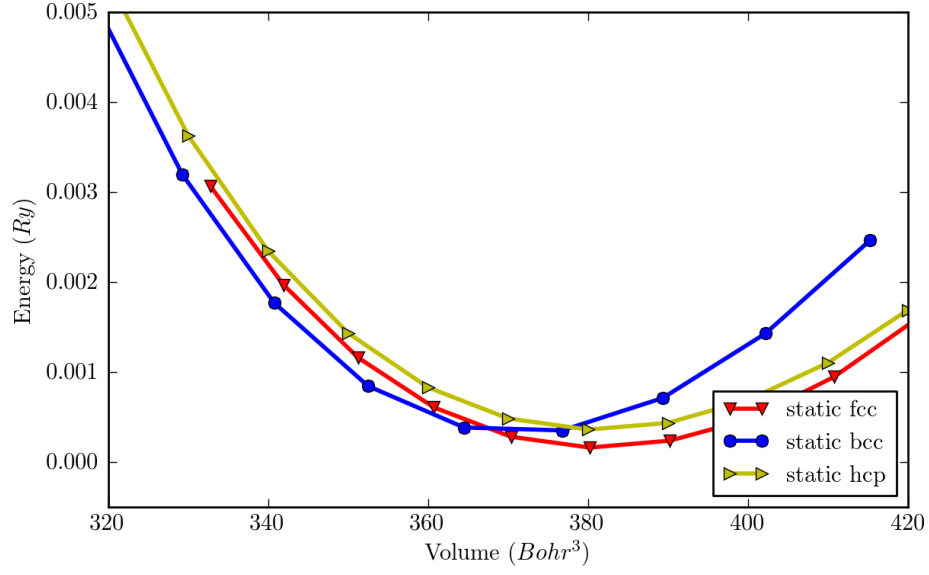


Figure 3.4: Zoomed view of Fig. 3.3 to verify that fcc structure of Strontium has the lowest energy, i.e., most stable ground state.

3.4 Total Energy

The parameters generated from the TB method are used to replicate the LAPW total energies for fcc and bcc. Total energies are also generated for sc, hcp and dia structures. In case of fcc, bcc, and sc, the parameters reproduce the energies to be identical to the LAPW-GGA *ab initio* inputs as show in Fig. 3.3.

As expected, sc and dia energies are higher than that of fcc and bcc, and are shown in Fig. 3.3. Fig. 3.4 shows a zoomed version of Fig. 3.3 to show and confirm that fcc is indeed the lattice structure with lowest energy and hence, the ground state stable structure. The hcp total energies were generated for different tetragonal strains by varying the c/a ratio values from 0.80 to 2.95. The structure with the c/a ratio of 1.65 is proved to be the lowest in energy but higher than that of fcc and bcc.

Keeping the volume constant, the energy is plotted as the tetragonal strain has been varied. This tetragonal distortion is represented as a Bain path, which is shown in

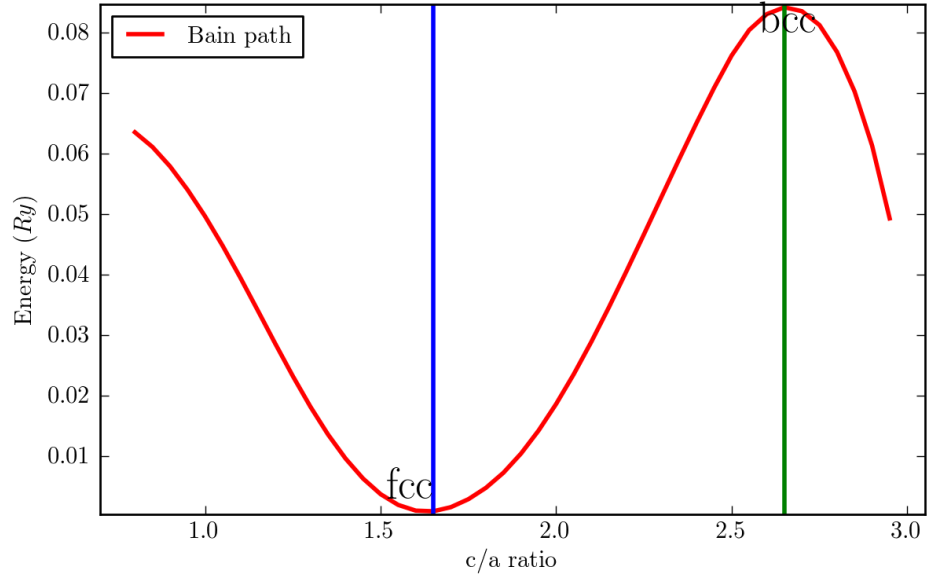


Figure 3.5: Bain path for Strontium at experimental equilibrium volume of 740 Bohr^3 .

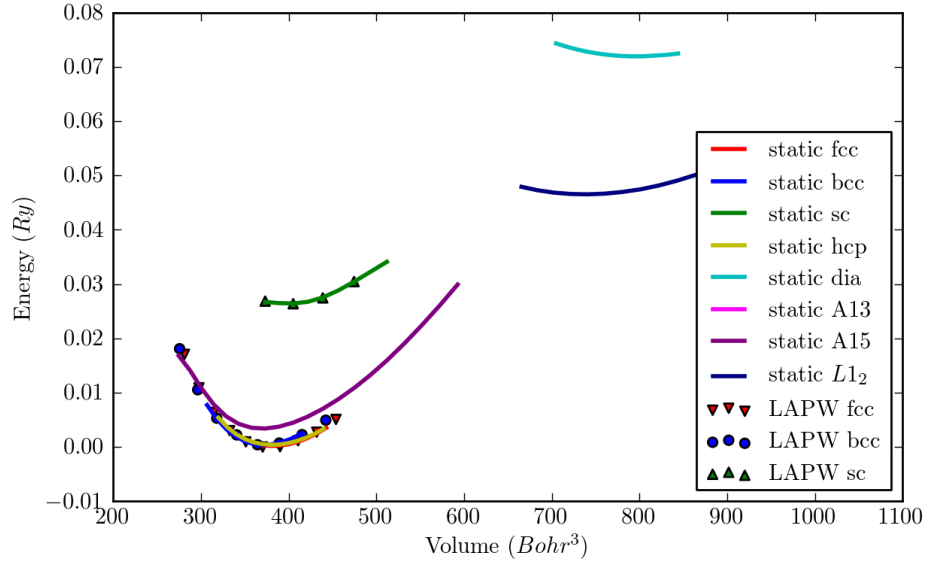


Figure 3.6: Total energies for fcc, bcc, sc, hcp, dia, A13, A15, and L_{12} structures of Strontium predicted using the NRL-TB parameters.

Fig. 3.5 and is explained in detail by Alippi et al. [51]. The Bain path shows a phase change from fcc to bcc when crystal is compressed as shown by the authors of [37, 51]. A study of metastable states in strained monoatomic cubic crystals [39] has shown that

Table 3.2: Ground state minimum energies of fcc, bcc, sc, hcp, dia, A13, A15, and $L1_2$ structures predicted using NRL-TB parameters compared with other calculated results.

	Structure	This work	EAM Potential ^a	NRL-TB using LDA ^b
		(eV)	(eV)	(eV)
fcc fitted	A1	0	0	0
bcc fitted	A2	0.0025	0.007	0.0285
sc fitted	A_h	0.3573	0.340	0.2993
hcp	A3	0.0027	0.007	0.0136
diamond	A4	0.9771	1.010	0.9932
βMn	A13	0.6864		0.0435
βW	A15	0.0435		0.0190
$AuCu_3$	$L1_2$	0.6310		0.3020

^aReference [36]

^bReference [2]

the bcc minimum is at $c/a = 0.707$.

Fig. 3.6 shows the total energies of other structures like $L1_2$, A13, and A15 predicted by the NRL-TB Hamiltonian. Table 3.2 shows the minimum energies of each structure relative to fcc and how they compare with other calculated values in eV. Table 3.2 indicates that the TB parameters have been developed are transferable to account for structures that have not fitted, which is usually difficult to achieve with other approaches. EAM potential calculations give only relative energies for basic cubic structures.

3.5 Elastic Constants

We have applied varying strains to Sr using the NRL-TB parameters, and calculated the energy of the crystal under strain, using Eqs. (2.37) - (2.39). By calculating the slope of this relationship between energy and square of the strain e^2 , and after few conversions from atomic units to GPa, the elastic constant can be calculated. These are shown in Fig. 3.7.

Using NRL-TB, $C_{11} - C_{12}$ has been evaluated to have a value of 3.5 GPa and C_{44}

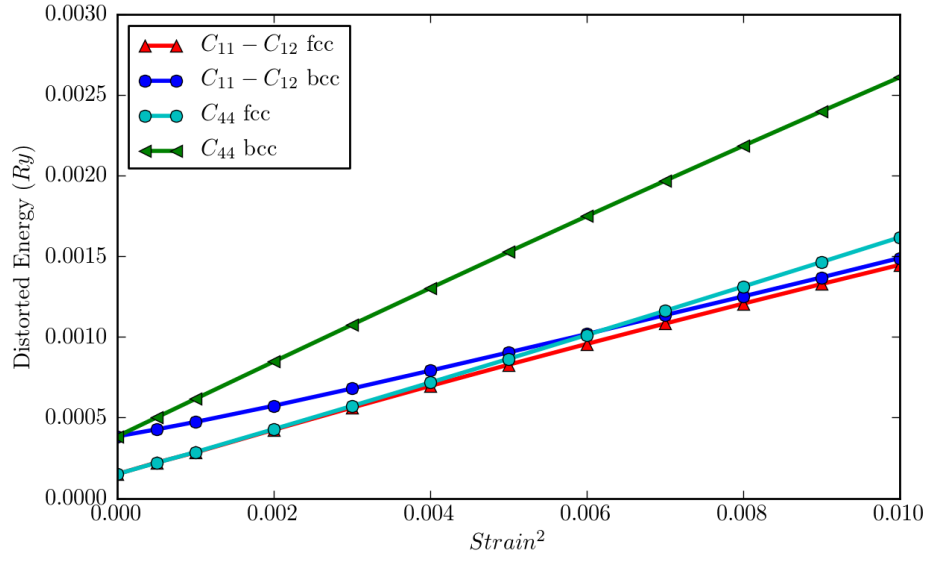


Figure 3.7: Linear relationship between distorted energy v. $strain^2$ of fcc and bcc structures of Strontium. Slopes of these lines help to calculate elastic constants $C_{11} - C_{12}$ and C_{44} .

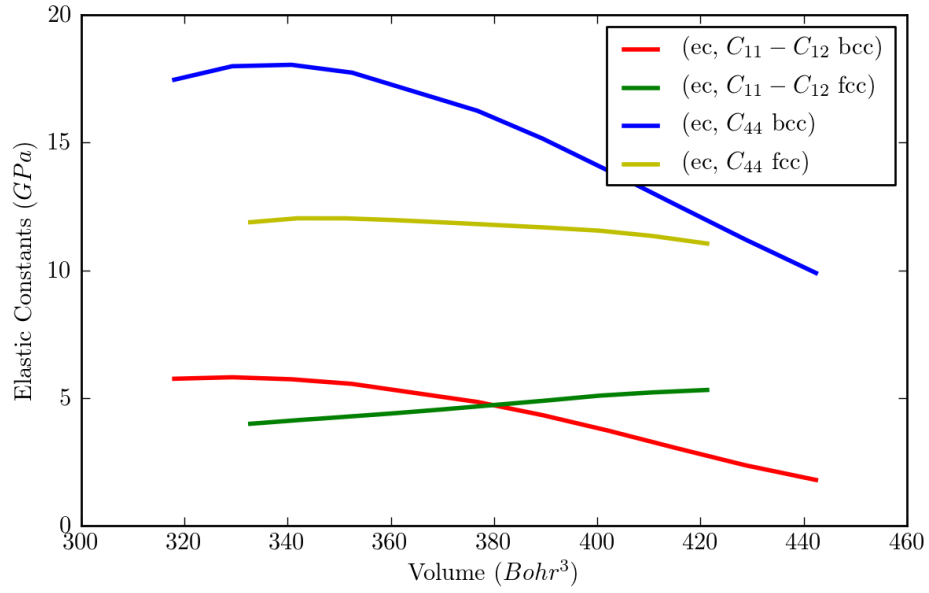


Figure 3.8: Elastic constants $C_{11} - C_{12}$ and C_{44} of fcc and bcc structures of Strontium vary with respect to change in volume.

has been deduced to be 14.5 GPa at equilibrium volume. The Springer Handbook [45]

Table 3.3: Comparisons of elastic constants $C_{11} - C_{12}$ and C_{44} of fcc and bcc structures of Strontium using NRL-TB results with experiment and other computational results.

	fcc		bcc	
	$C_{11} - C_{12}$ (GPa)	C_{44} (GPa)	$C_{11} - C_{12}$ (GPa)	C_{44} (GPa)
Present work TB using LAPW-GGA	3.50	11.34	5.24	14.02
Experiment ^a	3.25	7.41		
TB using LDA ^b	5.00	-3.00		
Experiment ^c	2.70	12.20		
EAM potential ^d	2.50	17.00		
Pseudopotential using VASP-LDA ^e	2.90	17.80		
Pseudopotential using VASP-GGA ^f	2.30	14.90		
FP LAPW ^g	2.05	5.90		
Pseudopotential ^h	2.60	8.90	3.70	6.90
FP LAPW ⁱ	1.80	3.50		
Experiment (bcc) ^j			2.60	8.90
Pseudopotential (bcc) ^k	0.20	14.90	4.70	11.10

^aReference [45]

^bReference [2]

^cReference [52]

^dReference [36]

^eReference [46]

^fReference [46]

^gReference [40]

^hReference [50]

ⁱReference [38]

^jReference [48]

^kReference [53]

presents values of $C_{11} = 10.94 \text{ GPa}$, and $C_{12} = 7.69 \text{ GPa}$, hence, $C_{11} - C_{12} = 3.25 \text{ GPa}$, which is within 2% of the calculated value as shown in Table 3.3. However, comparing C_{44} to experiment shows that calculated values are almost 50% larger. This is an improvement over negative values predicted using LDA input to the TB [2]. Since Sr is a soft material with small elastic constant values, it can be difficult to get accurate predictions for these values.

Other computations are in good agreement with experiment value with the exception of [38] using FP LAPW. NRL-TB calculations of elastic constant for Sr's bcc structure at equilibrium is greater than experiment [48] almost by a factor of 2. However, they are

in good agreement with values calculated using pseudopotential in [53].

The NRL-TB parameters estimate positive values for both $C_{11} - C_{12}$ and C_{44} , which predicts mechanical stability of a material. Also, $C_{11} - C_{12}$ and C_{44} are calculated for both fcc and bcc over a range of different volumes. The resultant graph in Fig. 3.8 shows an intersection between fcc and bcc values for C_{44} .

3.6 Energy Bands

Energy bands for fcc Sr, calculated using both LAPW-GGA and NRL-TB parameters, at ambient pressure is shown in Fig. 3.9. All eigenvalues have been shifted so that the Fermi level is at zero. The Fermi level E_f and two bands between W and L k-points cross at the same point confirming that Sr is a semi-metal.

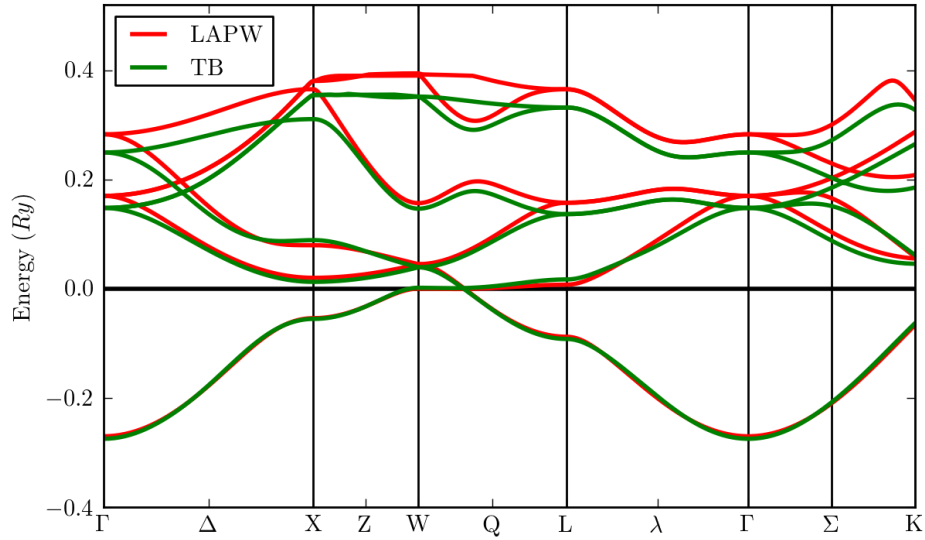


Figure 3.9: Comparison of energy bands of Strontium generated using LAPW-GGA and NRL-TB parameters, at equilibrium lattice constant $a = 11.4$ a.u. All eigenvalues have been shifted so that the Fermi level is at zero.

Below E_f , the electronic bands behave almost like free electrons. The d bands are above

the Fermi level E_f , hence, electronic wave contains a substantial mixture of d character. The TB fit is perfect below E_f and still very good above E_f . Energy bands are in good agreement with those calculated by Vasvari et al. [54], and Ley et al. [55].

3.7 Density of States

The DOS $N(E_f)$ for fcc has been determined using 89 k-points for both LAPW-GGA and NRL-TB. The ambient pressure DOS for LAPW and TB are shown in Fig. 3.10 and Fig. 3.11 respectively.

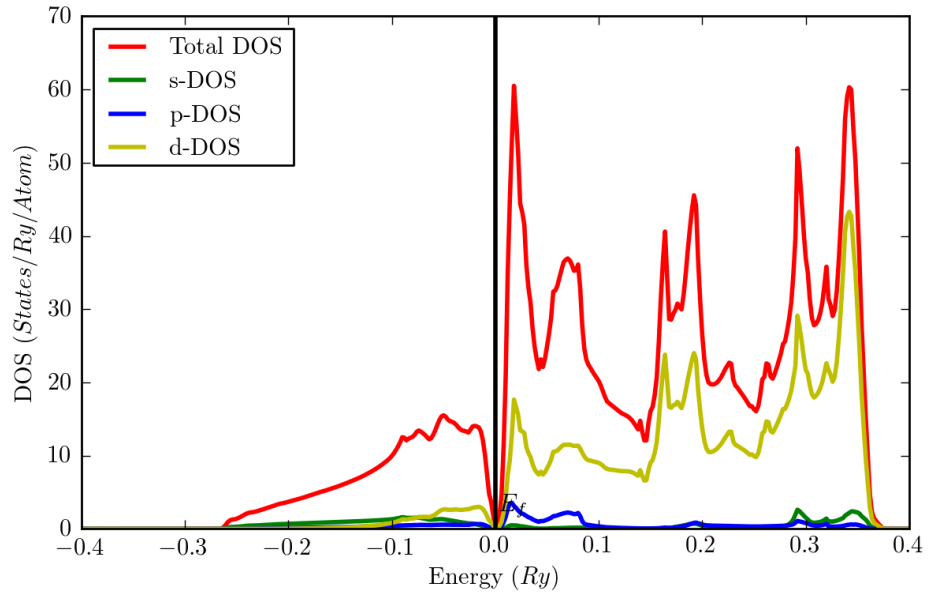


Figure 3.10: Density of States of Strontium calculated using LAPW-GGA at equilibrium lattice constant $a = 11.40$ a.u. All eigenvalues are shifted so that the Fermi level is at zero.

Similar to the shift in eigenvalues while plotting the band diagram, all eigenvalues are shifted for DOS values too, so that the Fermi level is at zero. It is observed that the peaks in both the LAPW-GGA DOS and the NRL-TB DOS occur in the same relative locations as shown in Fig. 3.13. The figures also show the decomposed angular momen-

tum that contribute to the total DOS. For LAPW, the decomposed angular momentum values are projections onto the muffin-tin spheres, and hence, are not an exact sum of the total DOS, which does not allow for a direct comparison with TB. For low energies, the l-DOS are very small, and the remaining part is outside the MT spheres, because the bands there are free-electron like (plane waves). On the other hand, well above E_f , the bands are almost exclusively d-like, which are localized inside the MTs, and this is why the d-DOS is almost equal to the total DOS. A dip is observed very close to E_f , which is approximately zero, confirming again that Sr is a semi-metal. Below E_f , the electronic structure is simple and behaves almost like free electrons. Above E_f , presence of the empty d band complicates the electronic structure. The exact values at E_f are shown in Table 3.4 along with decomposed angular momentum values.

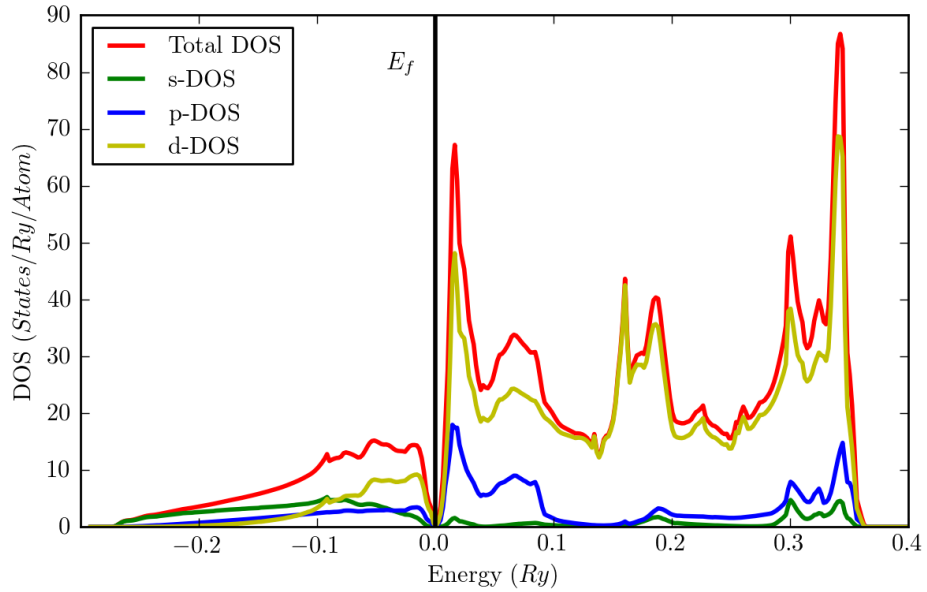


Figure 3.11: Density of States of Strontium calculated using NRL-TB parameters at equilibrium lattice constant $a = 11.40$ a.u. All eigenvalues are shifted so that the Fermi level is at zero.

From Table 3.4, it can be observed that both the LAPW and TB total DOS, $N(E_f)$, is practically zero confirming the semi-metallic behavior of Sr. It is also seen from Ta-

Table 3.4: Comparisons of LAPW-GGA and NRL-TB results of Density of States calculations of Strontium at E_f at equilibrium volume.

	$N(E_f)$	s	p	d
	$(states/Ry/atom)$			
LAPW	0.30463	0.00076	0.01957	0.06010
TB	0.40010	0.00358	0.10814	0.28838

ble 3.5 that the LAPW-GGA results for smaller volumes than equilibrium give a clean gap, which could point to a possible semiconductor behavior under pressure. DOS is also determined for Sr, under pressure from 0.0 – 4.4 GPa. The DOS obtained when Sr is compressed to lattice constant=10.60 a.u. is as shown in Fig. 3.12. Again, eigenvalues have been shifted so that Fermi level is zero.

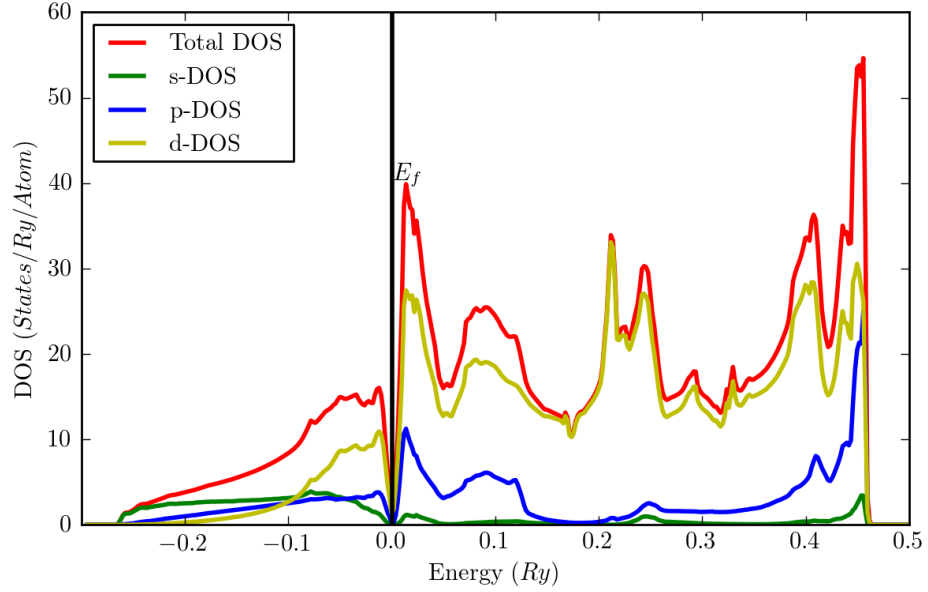


Figure 3.12: Density of States of Strontium calculated using NRL-TB parameters at lattice constant $a = 10.60$ a.u.

Band structure away from equilibrium have not been fitted well and therefore, only

Table 3.5: Comparisons of LAPW-GGA and NRL-TB results of Density of States calculations of Strontium for various lattice constants.

Lattice Constant	$N(E_f)$	s	p	d
<i>(states/Ry/atom)</i>				
LAPW-GGA				
10.6	0.00000	0.00000	0.00000	0.00000
10.8	0.00000	0.00000	0.00000	0.00000
11.0	0.00000	0.00000	0.00000	0.00000
11.2	0.00026	0.00000	0.00002	0.00006
11.4	0.00983	0.00001	0.00070	0.00209
11.6	0.37991	0.00099	0.02242	0.08433
11.8	0.92272	0.00278	0.05667	0.18571
12.0	2.75217	0.01102	0.19663	0.46082
12.2	4.86491	0.01947	0.38893	0.61979
NRL-TB				
11.2	0.20583	0.00248	0.05961	0.14373
11.4	0.45142	0.00491	0.13367	0.31284
11.6	0.34635	0.00314	0.10232	0.24088

NRL-TB results for lattice constants 11.2 – 11.6 Bohr have been presented in Table 3.5. It shows the effects of change of lattice constant on the DOS, and its decomposed angular momentum values. The table also illustrates decomposed angular momentum values generated using LAPW and TB parameters. For DOS values generated using LAPW, the decomposed angular momentum values below equilibrium lattice constant are zero, indicating the presence of free electrons. The Fermi level E_f increases, as the volume decreases, predicting non-metallic nature of Sr under pressure. On the other hand, for the expanded lattice (lattice parameters greater than 11.8 Bohr) Sr becomes clearly a metal as seen in Table 3.5. Similar behavior is observed in DOS values generated by TB parameters, however, the decomposed angular momentum values below equilibrium lattice constant are very close to zero, not exactly zero as in LAPW.

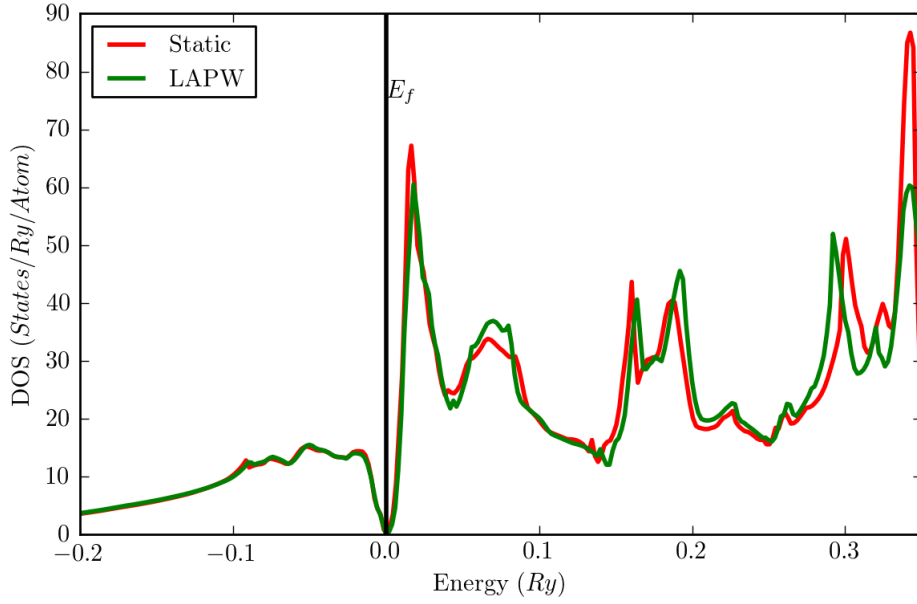


Figure 3.13: Density of States of Strontium calculated using LAPW inputs and NRL-TB parameters at lattice constant $a = 11.40$ a.u.

3.8 Tight-Binding Molecular Dynamics

The parameters generated using the NRL-TB method are used with the TBMD package by Kirchhoff et al. [29] to determine thermodynamic properties as explained in Chapter 2 Section 2.16. Using the parameters generated from the fit, TBMD has been performed on temperatures ranging from $100K - 1000K$ for both fcc and bcc structures, and the super-cell used consisted of 343 atoms by replicating a single cell 7 times. Each temperature calculation has been run for 2000 steps. Figure 3.14 shows the equilibration for target temperature of 300K.

We expected the MD to break at melting point of Sr, which is 1042K, however, there is a phase change in Sr from fcc to bcc around 830K as measured by Jayaram et al. [35] and results using fcc structure reflect this with an abrupt stop after 800K. The MD runs for the bcc structure aborted after 600K. Temperature values of each TBMD run is presented in Table 3.6. However, Wax et al. [56] were able to predict melting

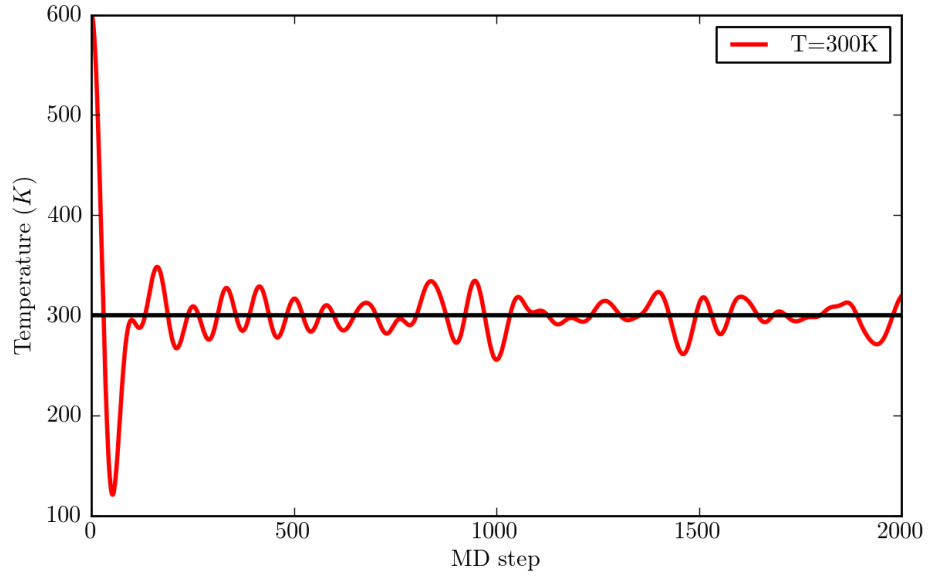


Figure 3.14: Equilibration of Strontium at target $T = 300K$.

temperature of 1029 K using molecular dynamics simulations on liquid phase of Sr.

Table 3.6: Results of TBMD on fcc and bcc structures of Strontium.

Target Temperature (K)	Equilibration Temperature (K)	
	fcc structure	bcc structure
100	109.40	89.945
200	217.02	188.57
300	319.37	286.22
400	403.93	378.46
500	482.62	478.61
600	588.49	609.79
700	694.91	-
800	816.17	-

3.9 Mean Square Displacement

We have used the atomic positions generated by the MD simulations performed for several temperatures at the corresponding experimental lattice constants to compute the atomic MSD, which is an indication of atomic diffusivity, i.e., distance travelled by a particle over a time interval. It is an average of atomic positions, which are generated by TBMD over all atoms and time steps.

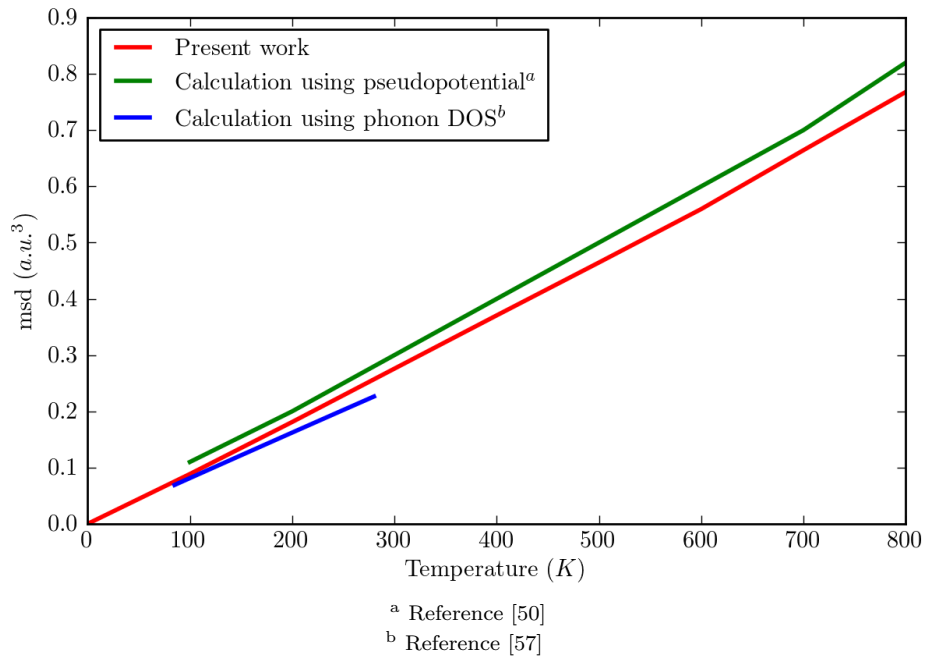


Figure 3.15: Mean square displacement for Strontium.

The MSD for each temperature has been calculated in atomic units and is shown in Fig. 3.15, and this value is key in calculating the Debye-Waller factor. Calculated values are in good agreement with those predicted by Baria et al. [50] using pseudopotentials, and also that those calculated by Peng et al.[57]. Comparisons with these calculations are also shown in Fig. 3.15.

3.10 Vacancy Formation Energy

The VFE for Sr has been tested via a relaxed super-cell method with conjugate gradient approximation, in which the energy of a cell with a complete lattice is compared to a lattice in which one atom has been removed. The VFE indicates the stability of the structure due to the loss of an atom; a positive value means that the structure is more stable in the full lattice configuration.

Using the NRL-TB parameters, the VFE has been calculated to be 1.03 eV. This is corroborated by the calculations using EAM potential [36] as 0.97eV. Other calculations, using a jellium model, cite much lower values at 0.66 eV [58].

3.11 Enthalpy

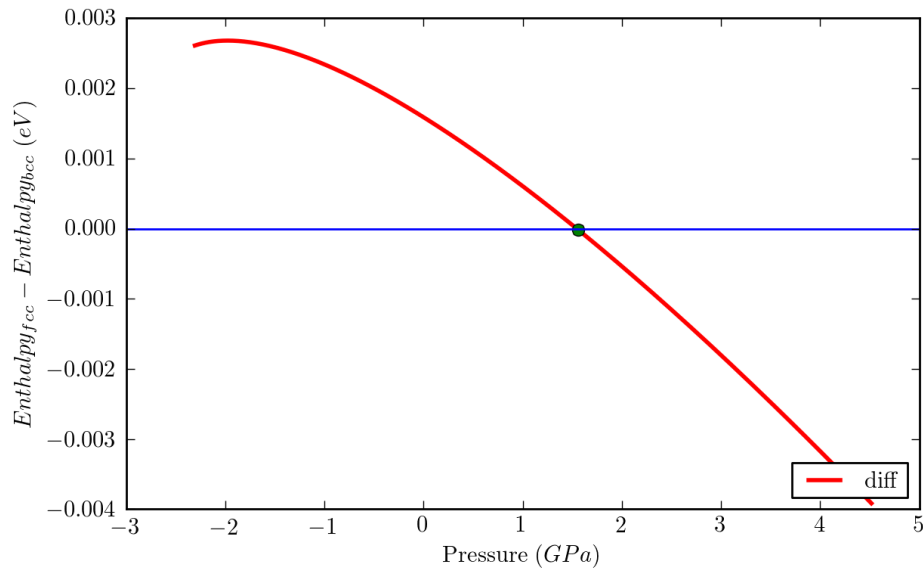


Figure 3.16: Difference in Enthalpy for Strontium plotted against pressure in GPa.

Enthalpy has been calculated from the equation $H(P) = E + PV$ as explained in Chapter 2, Section 2.19, for both fcc and bcc structures and the difference between enthalpies for fcc and bcc is plotted with respect to pressure in GPa, shown in Fig. 3.16. An intersection with the zero difference line is found at 1.55 GPa at a volume of 343 Bohr^3 . This intersection indicates a phase change, and it is close to the 3.5 GPa transition pressure

(at room temperature) experimental phase change measured by Andersen et al. [49]. In comparing Burgers and Bain deformation mechanisms, Katzke et al. [59] also have confirmed this transition pressure to be 3.5 GPa. Skriver [43] also calculated it to be slightly higher at 3.8 GPa. FP LAPW pseudopotential methods [40] calculated a range at which fcc to bcc transition occurs between 1.95 and 2.20 GPa. While this calculated value seems to be almost 50% smaller than experimental and calculated values, one should note that Sr is a very soft material and hence, transition pressures are very much smaller than transition metals or semiconductors.

3.12 Phonon Frequencies

We have used the NRL-TB parameters to calculate phonon frequencies at high symmetry q-points using the frozen phonon approximation method. Table 3.7 lists phonon frequencies in THz, calculated at experiment equilibrium of 11.5 Bohr. The calculated values are in good agreement with experiment [52] and other calculations using EAM potential [36].

We have also calculated the phonon frequencies at lattice constants varying from 11.2 – 11.8 Bohr. As pressure increases, i.e., lattice constant decreases, the frequencies show an upward trend as indicated in Fig. 3.17. The values of the phonon frequencies in THz are tabulated in Table 3.8.

Table 3.7: Phonon frequencies of equilibrium fcc structure of Strontium compared with other calculated values.

	This work	Expt ^a	EAM ^b	Pseudopotential ^c	Murrell and Mottram potential ^d
(THz)					
X_3	3.56	3.17	3.19	2.80	3.20
X_5	2.32	2.48	2.46	2.00	2.20
L_2	3.52	3.08	3.03	2.80	3.00
L_3	1.49	1.74	1.42	1.20	1.50
W_2	2.31	2.57	2.46		
W_5	3.04				
Δ_1	2.32	1.90		1.60	1.90
Δ_5	1.62	1.50		1.30	1.20
Σ_1	2.92	2.70		2.40	2.60
Σ_2	1.46	1.40		1.70	1.50
Σ_3	2.49	2.40		2.20	2.20

^aReference [52]

^bReference [36]

^cReference [60]

^dReference [61]

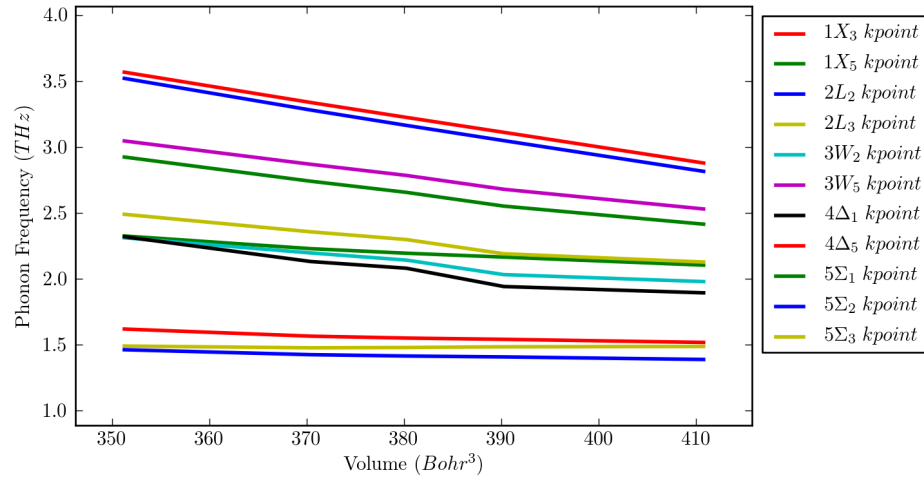


Figure 3.17: Variation of Phonon frequencies of Strontium with respect to pressure.

Table 3.8: Variation of Phonon frequencies of fcc structure of Strontium with respect to change in volume.

Lattice constant (<i>Bohr</i>)	11.20	11.40	11.50	11.60	11.80	Experiment ^a at 11.50
q-points	(THz)					
X_3	3.56	3.33	3.23	3.11	2.88	3.17
X_5	2.32	2.23	2.19	2.16	2.10	2.48
L_2	3.52	3.28	3.17	3.04	2.81	3.08
L_3	1.49	1.47	1.47	1.48	1.48	1.74
W_2	2.31	2.19	2.14	2.03	1.98	
W_5	3.04	2.87	2.79	2.68	2.53	
Δ_1	2.32	2.13	2.08	1.94	1.89	1.9
Δ_5	1.62	1.56	1.55	1.54	1.51	1.5
Σ_1	2.92	2.74	2.66	2.55	2.41	2.7
Σ_2	1.46	1.42	1.41	1.40	1.38	1.4
Σ_3	2.49	2.35	2.30	2.19	2.12	2.4

^aReference[52]

3.13 Summary

To summarize, the NRL-TB method has successfully generated transferable parameters for Sr, which successfully predict total energies of structures that were not included in the fit. Also, mechanical properties like elastic constants and bulk modulus provide a good agreement with experiment. The DOS, enthalpy and phonon frequencies are a good estimate. Large calculations including TBMD, MSD and VFE were performed with much smaller computational time than with first principles.

Chapter 4: Alkaline Earth Metal: Calcium

4.1 Calcium

Calcium (Ca) is the fifth most abundant material on the earth's crust and hence, has been extensively studied compared to other alkaline earth metals. It is a metal, which is very soft material and is extremely reactive. The Naval Research Laboratory (NRL)-Tight-Binding (TB) method using Local Density Approximation (LDA), which was applied to transition and noble metals by Mehl et al. [2], also included alkaline earth metals Strontium (Sr) and Ca. However, elastic constants predicted were not in good agreement with experiment, but unlike Sr, the values were positive for Ca. This poor agreement with experiment, inhibited further study of properties using other methods such as molecular dynamics, and hence, the calculations in this work are reexamined using Linear Augmented Plane Wave (LAPW)-Generalized Gradient Approximation (GGA).

Embedded Atom Method (EAM) potential calculations presented by Sheng et al. [36] for 14 face centered cubic (fcc) metals include Ca, and are in good agreement with results presented in this study. McCaffrey et al. [62] have studied effects of pressure on electronic structure of Ca, using self consistent glsapw calculations. Vasvari et al. [54] have calculated electronic structure of 3 alkaline earth metals using pseudopotentials. However, authors of both [62] and [54] did not calculate total energy. Blaha et al. [63] and Ley et al. [55] have provided both experimental results using X-ray spectrometry and also *ab initio* method calculations using pseudopotentials, and Jan et al. [64] have performed similar calculations using the Linear Muffin-Tin Orbitals (LMTO) method.

Ca in its ground state, i.e., at room temperature and pressure has a fcc structure. Increase in pressure and temperature causes it to transform to body centered cubic

(bcc) and eventually to simple cubic (sc). Olijnyk et al. [42] have predicted that the fcc to bcc transformation occurs at 19.50 GPa, and that to sc occurs at 32 GPa. These transitions are experimentally verified using X-ray diffraction by Yuki Nakamoto et al. [65]. Also, Lei et al. [66] used LAPW-GGA to study superconductivity of Ca under pressure, and predicted the transition pressure of Ca from fcc to bcc to be 10 GPa.

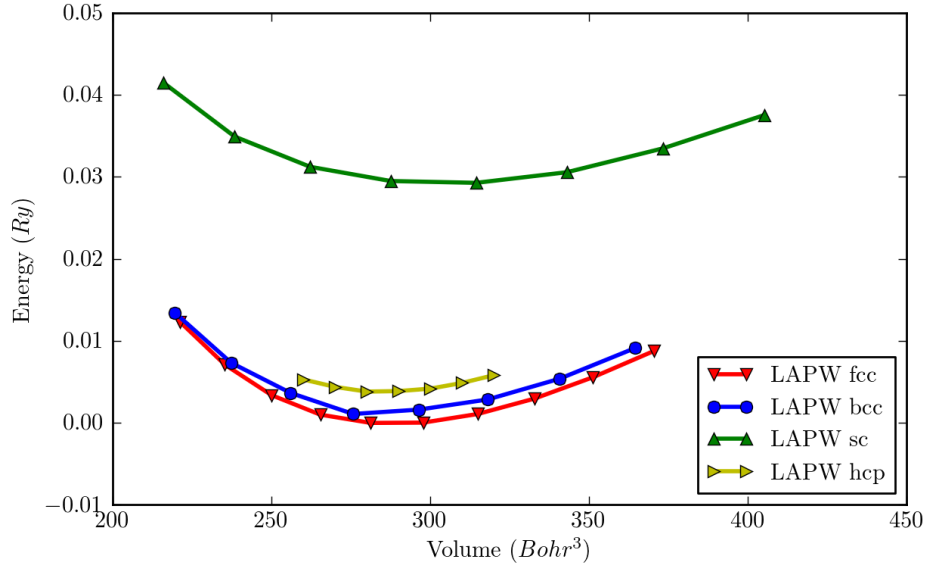


Figure 4.1: Total energies of Calcium for fcc, bcc, sc, and hcp structures generated using LAPW-GGA.

This chapter describes the results of LAPW-GGA calculations of several lattice structures of Ca as a function of pressure. These energies are input to the NRL-TB fit, which gives a set of 97 parameters. These TB parameters are then used to predict total energies for the following lattice structures: bcc, fcc, sc, hexagonal close packed (hcp), and diamond. Using these TB parameters, predictions are made on mechanical properties like elastic constants for both bcc and fcc structures, band structure, Density of States (DOS), electronic specific heat coefficient, phonon frequencies, enthalpy, Molecular Dynamics (MD), Mean Square Displacement (MSD), and Vacancy Formation Energy (VFE).

4.2 LAPW-GGA

Table 4.1: Comparisons of Calcium’s lattice constant and bulk modulus with experiment and other computational results.

	Lattice Constant (<i>Bohr</i>)	Bulk Modulus (<i>GPa</i>)
Present work LAPW-GGA input	10.488	16.2
Reference handbook ^a	10.545	19.6
TB using LDA ^b	10.091	19.0
APW ^c	10.526	17.2
LMTO ^d	10.545	15.0
FP LAPW ^e	10.186	19.2
Pseudopotential using VASP ^f	10.016	18.9
EAM potential ^g	10.545	21.0

^aReference [45]

^bReference [2]

^cReference [44]

^dReference [64]

^eReference [38]

^fReference [46]

^gReference [36]

We have initially performed LAPW-GGA calculations to generate total energies for only fcc, bcc and sc, which are fitted using the TB code. However, the TB parameters generated from this fit, showed in static, hcp as the ground state structure instead of fcc. Hence, LAPW-GGA inputs are generated for hcp, and which have showed that indeed fcc is the equilibrium structure. This is shown in Fig. 4.1. For fcc, energies were generated as a function of lattice constant and are in the range of 10.60 – 12.20 *Bohr*, for bcc they are in the range of 8.20 – 10.00 *Bohr*, and for sc 7.00 – 7.80 *Bohr*. For hcp, energies are generated as a function of volume of 260 to 320 *Bohr*³ for *c/a* ratios of 1.55 to 1.75. The lattice with *c/a* = 1.65 is found to have the lowest energy among hcp, and these values are used as input to the NRL-TB code.

The equilibrium lattice constant calculated for fcc is 10.488 *Bohr*, which is 0.54% smaller than the experiment value as shown in Table 4.1. This is much closer to experiment than previous LDA calculations presented by Mehl et al. [2]. Also, the bulk modulus

calculated to be 16.2 GPa is a closer match to the experimental value, which is 19.6 GPa from the Springer Handbook [45]. Other calculated values of bulk modulus vary from 14 to 21 GPa as shown in Table 4.1.

4.3 Tight-Binding

Non-orthogonal TB parameters, as in Appendix A.2, are generated to fit total energies of fcc, bcc, sc and hcp. For fcc, bcc, sc and hcp, 55, 27, 18, and 7 volumes have been fitted respectively. The fit generated is a close match with the LAPW-GGA values as shown in Fig. 4.2. The total RMS error for the total energies is 0.000573 Ry and that of the bands averages around 0.014 Ry.

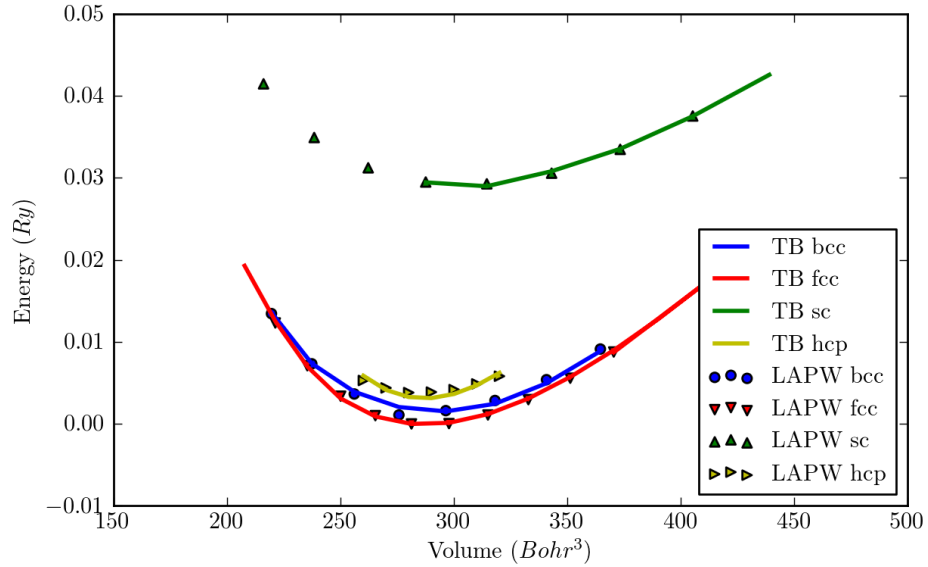


Figure 4.2: Total energies of fcc, bcc, sc, and hcp structures of Calcium obtained from NRL-TB in comparison with input values from LAPW-GGA.

As expected, fcc has the lowest total energy and hence, in agreement with experiment that it is the stable lattice structure. The lattice constant corresponding to the lowest energy is 10.480 Bohr, which is 0.54% smaller than the experiment value of 10.545 Bohr.

The lowest lattice constant used in the fit for fcc is 8.40 Bohr, which is approximately 82% of the equilibrium lattice constant and hence, the TB parameters may be used as an input to the Tight-Binding Molecular Dynamics (TBMD) program.

4.4 Total Energy

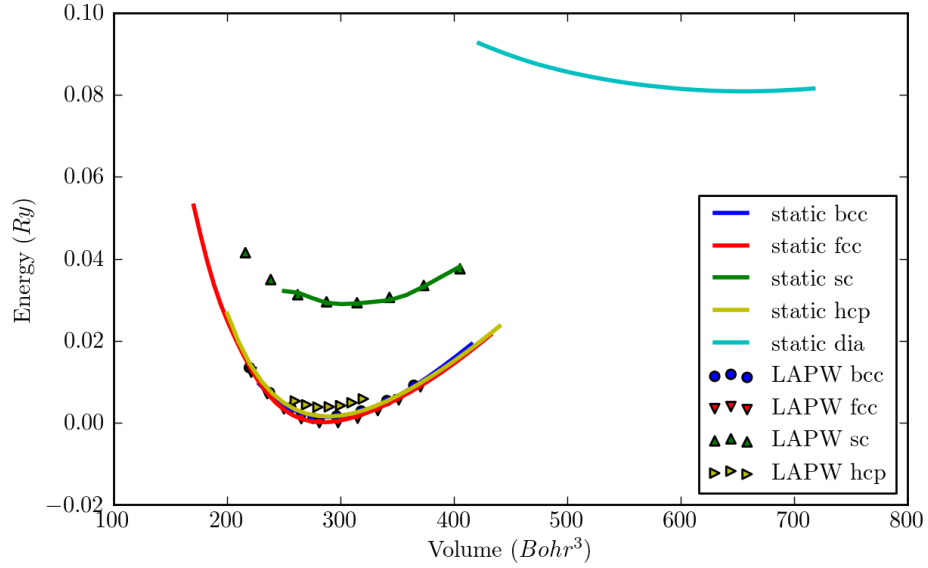


Figure 4.3: Total energies of fcc, bcc, sc, hcp, and dia structures of Calcium generated using the NRL-TB parameters compared with input values of fcc, bcc, and sc energies generated using LAPW-GGA.

The TB parameters generated from the TB method are used to replicate the LAPW total energies for fcc and bcc. Total energies are also generated for sc, hcp, and dia structures. In case of fcc, bcc, and sc, the TB parameters have reproduced the energies nearly identical to the LAPW-GGA *ab initio* inputs as show in Fig. 4.3.

As expected, sc and dia energies are higher than that of fcc and bcc, and are shown in Fig. 4.3. Fig. 4.4 shows a zoomed version of Fig. 4.3 to show and confirm that fcc is indeed the lattice structure with lowest energy and hence, the ground state stable struc-

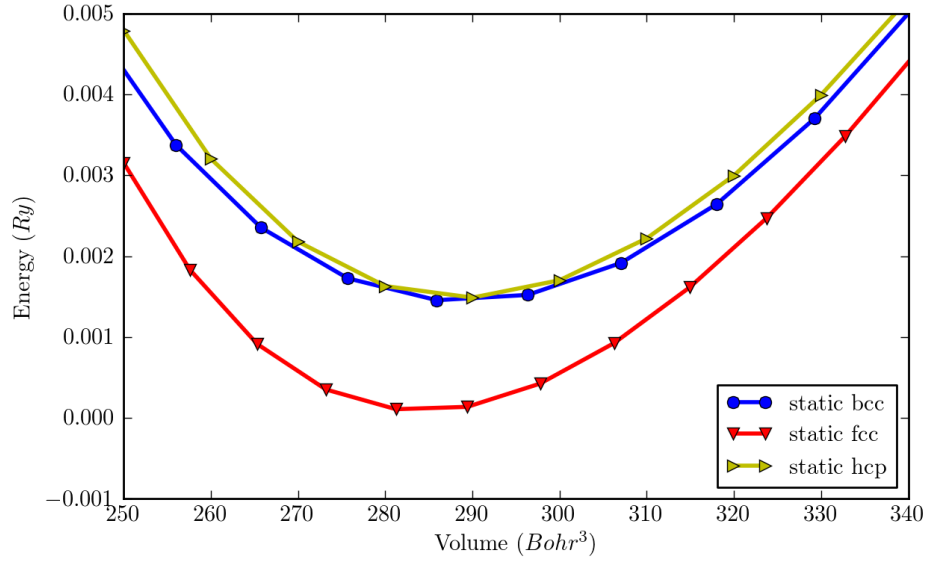


Figure 4.4: Zoomed view of Fig. 4.3 to verify that fcc structure of Calcium has the lowest energy, i.e., the most stable ground state.

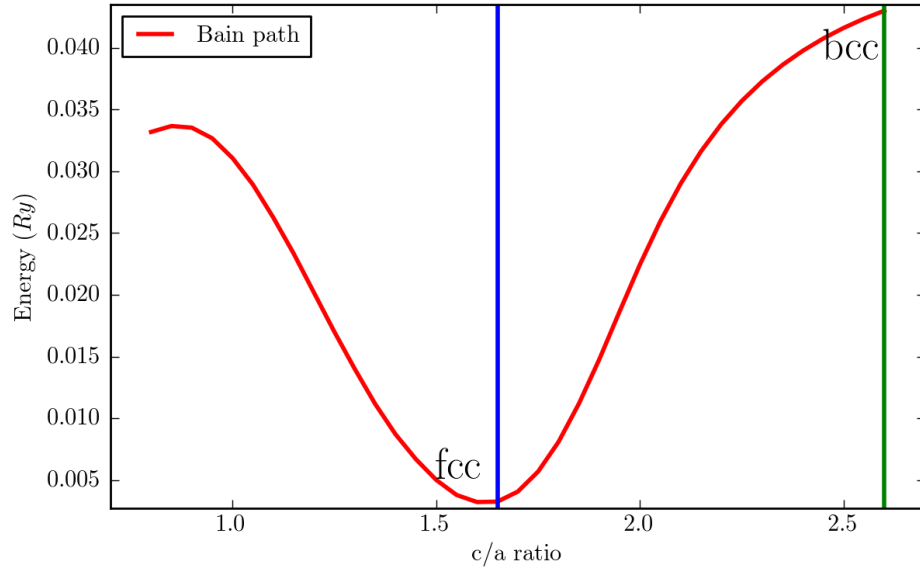


Figure 4.5: Bain path of Calcium at equilibrium lattice constant.

ture. The hcp total energies are generated for different tetragonal strains by varying the c/a ratio values from 0.80 to 2.95. The structure with the c/a ratio of 1.65 gives the lowest energy, which is higher than the fcc, but lower than the bcc.

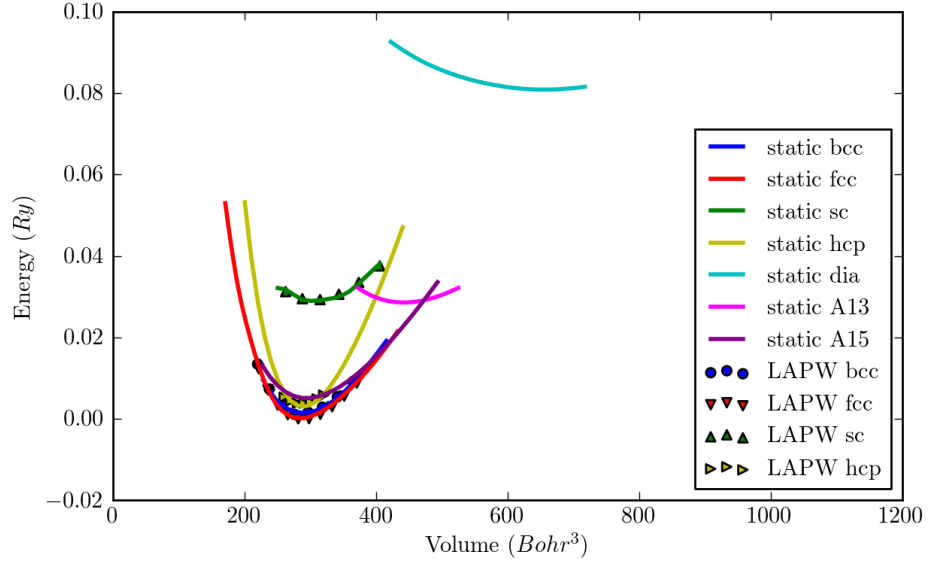


Figure 4.6: Total energies of A13, A15, and $D0_3$ structures of Calcium predicted using parameters generated by NRL-TB.

Table 4.2: Ground state minimum energies of fcc, bcc, sc, hcp, dia, A13, A15, and $D0_3$ structures predicted using NRL-TB parameters compared with other calculated results.

	Structure	This work (eV)	EAM Potential[36] (eV)
fcc fitted	A1	0	0
bcc fitted	A2	0.018557900	0.009
sc fitted	A_h	0.392659902	0.395
hcp fitted	A3	0.038236665	0.003
dia	A4	0.953769319	1.050
βMn	A13	1.162960240	
βW	A15	0.073623017	
$AlFe_3$	$D0_3$	0.860336861	

The energy of hcp lattice is plotted keeping the volume constant as the tetragonal strain is varied. This tetragonal distortion is represented as a Bain path and shown in Fig. 4.5 and is explained in detail by authors of [51]. The Bain path shows a phase change from fcc to bcc when crystal is compressed [37], and varies from that presented by Sliwko et

al. [38] for equilibrium lattice which shows a shallow minimum at $c/a = 1$.

Total energies of other structures not included in fit, like A13, A15, and $D0_3$ are calculated, and are as shown in Fig. 4.6. Table 4.2 shows the stable energies of each structure relative to fcc, and how they compare with other calculated values in eV.

4.5 Elastic Constants

Fig 4.7 shows the variation of the elastic constants $C_{11} - C_{12}$ and C_{44} with the square of the strain (x^2) for both the fcc and bcc structures. There is a linear relationship for the stable fcc structure, while the non-linear behavior for the bcc $C_{11} - C_{12}$ is not surprising, since bcc is not the ground state. The slopes of these graphs are used to determine the actual elastic constants listed in Table 4.3. At equilibrium volume, elastic constants $C_{11} - C_{12}$ and C_{44} were found to have a value of 5.79 GPa and 17.85 GPa respectively.

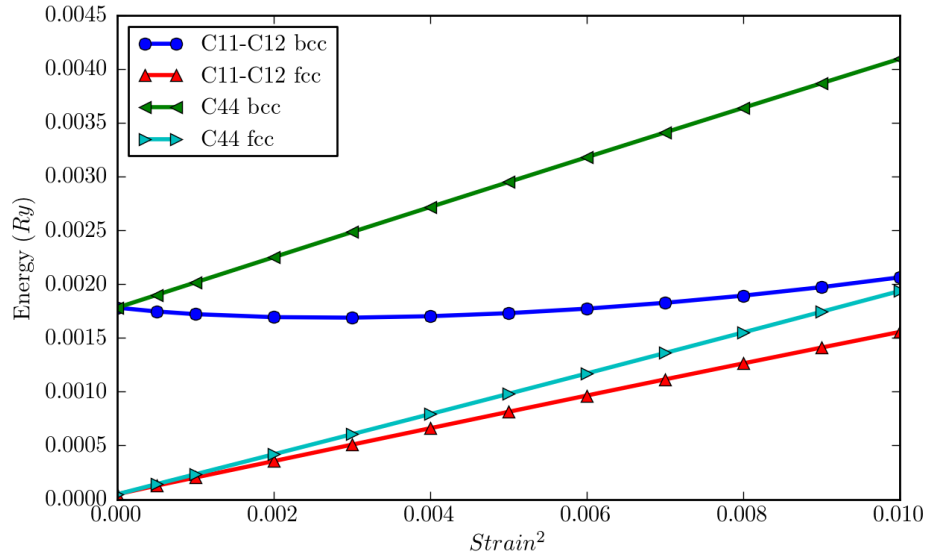


Figure 4.7: Linear relationship between distorted energy v. $strain^2$ of fcc and bcc structures of Calcium. Slopes of these lines help to calculate elastic constants $C_{11} - C_{12}$ and C_{44} .

Table 4.3: Comparisons of elastic constants $C_{11} - C_{12}$ and C_{44} of fcc and bcc structures of Calcium using NRL-TB results with experiment and other computational results.

	fcc		bcc	
	$C_{11} - C_{12}$ (GPa)	C_{44} (GPa)	$C_{11} - C_{12}$ (GPa)	C_{44} (GPa)
Present work TB using GGA	5.79	17.85	1.43	23.72
Reference Handbook ^a	6.80	14.00		
LDA ^b	5.00	14.00		
Experiment ^c	9.80	16.30		
Experiment ^d	1.60	12.00	3.60	15.00
EAM Potential ^e	5.00	17.00		
Pseudopotential ^f	7.50	12.90	7.50	12.50
Pseudopotential ^g	2.10	5.10		
Pseudopotential using VASP ^h	8.00	17.20		

^aReference [45]

^bReference [2]

^cReference [67]

^dReference [68]

^eReference [36]

^fReference [50]

^gReference [69]

^hReference [46]

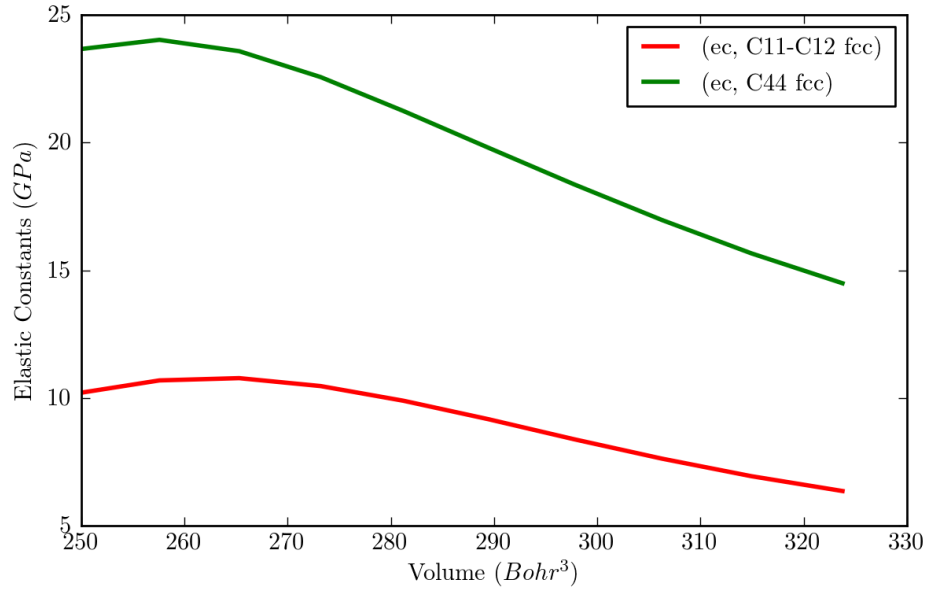


Figure 4.8: Variation of fcc structures of Calcium's $C_{11} - C_{12}$ and C_{44} elastic constants with respect to volume.

Comparisons with various experiment and other calculations are as shown in Table 4.3. Unlike Sr, these values are not a huge improvement over values predicted using LDA [2]. Computational values of $C_{11} - C_{12}$ are a much better match than those presented in [67] and [36] as 9.8 GPa and 5.0 GPa respectively. Predictions by Heiroth et al. [68] are much lower at 1.6 GPa. Various experiments and calculations have yet to reach a close agreement, since Ca is a very soft material.

For fcc structure, mechanical stability has been calculated over a range of different volumes as shown in Fig. 4.8.

4.6 Energy Bands

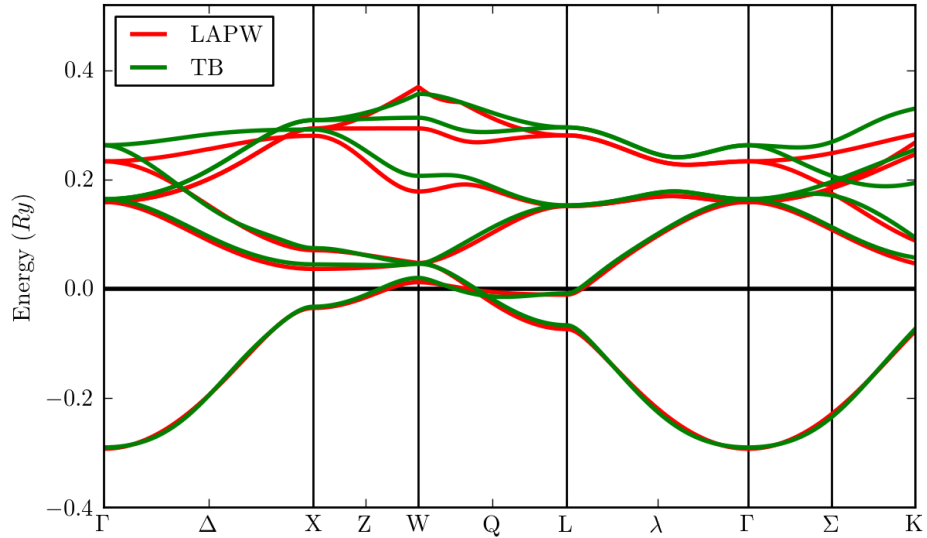


Figure 4.9: Comparison of energy bands of Calcium using LAPW-GGA and NRL-TB parameters, at equilibrium lattice constant $a = 10.40$ a.u. All eigenvalues have been shifted so that the Fermi level is at zero.

Energy bands for fcc Ca, calculated using both LAPW-GGA and NRL-TB parameters, at ambient pressure are shown in Fig. 4.9. Unlike Sr, a 2nd set of TB parameters have been generated, in which the RMS error of the band energies, and energy at only the equilibrium volume, are minimized. This second set of TB parameters, listed in Appendix A.3, gives a better agreement of energy bands as well as DOS. The energies

have been shifted so that Fermi level E_f is zero. Also, the electronic bands behave almost like free electrons below E_f . Energy bands generated using TB parameters are in very good agreement with the energy bands generated by LAPW below E_f , and less accurate for the unoccupied states as shown in Fig 4.9. They are in good agreement with those calculated by McCaffrey et al. [62], Vasvari et al. [54], Blaha et al. [63], Ley et al. [55] and Jan et al. [64].

4.7 Density of States

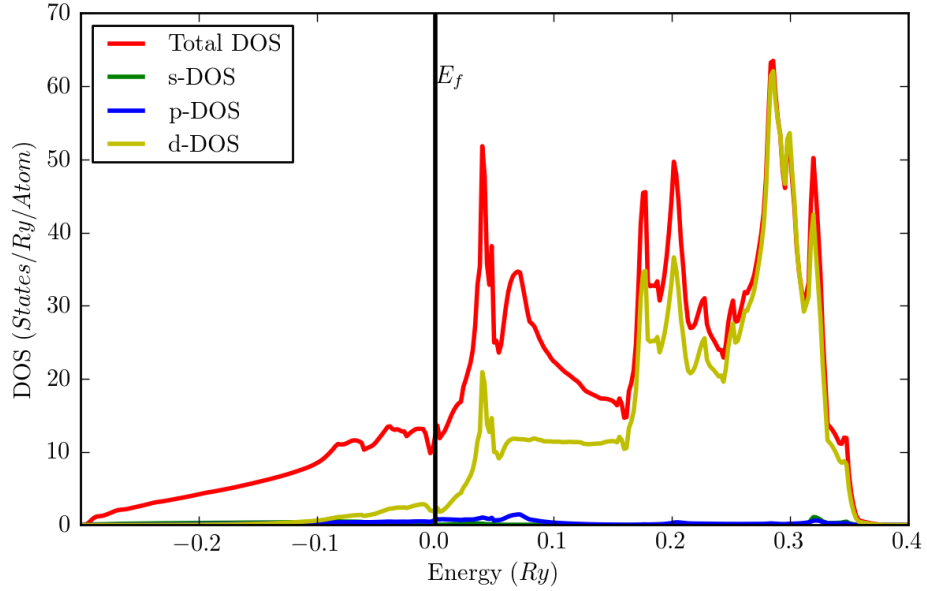


Figure 4.10: Density of States of Calcium calculated using LAPW-GGA at equilibrium lattice constant $a = 10.40$ a.u. All eigenvalues are shifted so that the Fermi level is at zero.

Similar to Sr, DOS for Ca has been calculated by the tetrahedron method [28], using 89 k-points, for both LAPW and TB. Fig. 4.10 shows the ambient pressure DOS of Ca, after shifting the eigenstate energies so that Fermi energy is zero. It is observed that the peaks in both the LAPW-GGA DOS and the NRL-TB DOS occur in the same relative locations as shown in Fig. 4.13. Also, shown are the decomposed angular momentum that contribute to the total DOS. The exact values are shown in Table 4.4 along with

Table 4.4: Comparisons of LAPW-GGA and NRL-TB results of Density of States calculations of Calcium at the Fermi level.

	$N(E_f)$	s	p	d
	<i>(states/Ry/atom)</i>			
LAPW	12.16077	0.044565	0.69894	2.086815
TB	11.51109	0.182600	5.36982	5.958670

the decomposed angular momentum values, which are projections onto the muffin-tin spheres and hence, are not an exact sum of the total DOS. For low energies, the l-DOS are very small and the remaining part is outside the MT spheres, because the bands at that position are free-electron like (plane waves). On the other hand, well above E_f the bands are almost exclusively d-like, which are localized inside the MTs and this is why the d-DOS is almost equal to the total DOS. The DOS generated using the NRL-TB parameters are shown in Fig. 4.11. Unlike Sr, there is no gap in the DOS at the Fermi level E_f for Ca, which confirms that Ca is a metal. Both, Jan et al. [64] and McCaffrey et al. [62] have calculated DOS of Ca, and are in good agreements with that shown in Fig. 4.13.

Using the value of DOS, the electronic specific heat coefficient of Ca is calculated to be $2.75 \text{ mJ}/(\text{mol deg}^2)$ using the Eq. (2.41), which is in good agreement with experimental value of γ from Kittel [25], which is $2.9 \text{ mJ}/(\text{mol deg}^2)$.

DOS has been determined by varying pressure from 0.0 – 4.4 GPa indicating that at ambient conditions, Ca has displayed metallic character. This is shown in Table 4.4. In Fig. 4.12, DOS of Ca calculated using TB parameters at lattice constant of 10.2 Bohr is shown. It is clearly indicated by the non-zero value of $N(E_f)$ that it is a metal.

The effects of change of lattice constant on the DOS, and its decomposed angular momentum values are shown in Table 4.5. The table also shows values generated using LAPW-GGA and NRL-TB.

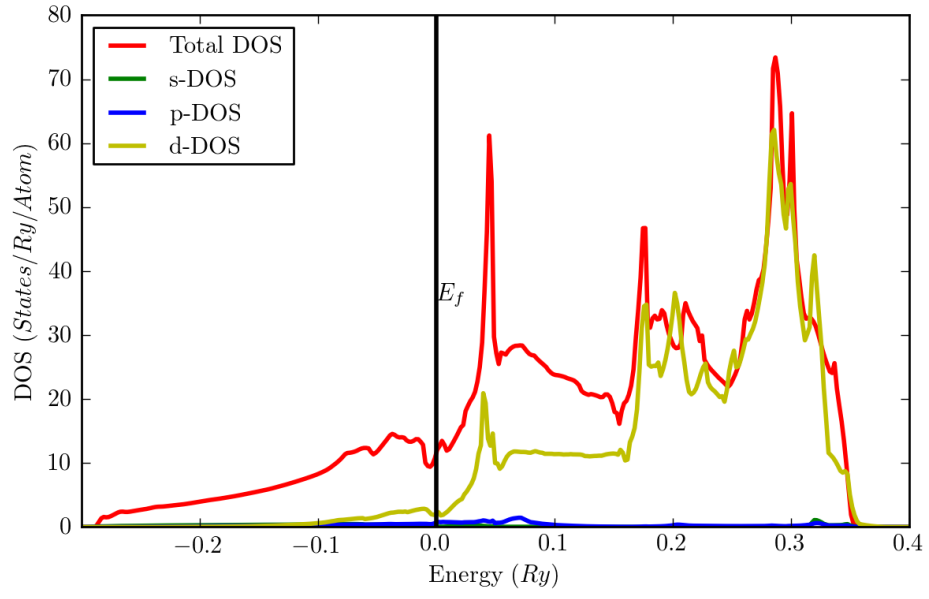


Figure 4.11: Density of States of Calcium calculated using NRL-TB at equilibrium lattice constant $a = 10.40$ a.u. All eigenvalues are shifted so that the Fermi level is at zero.

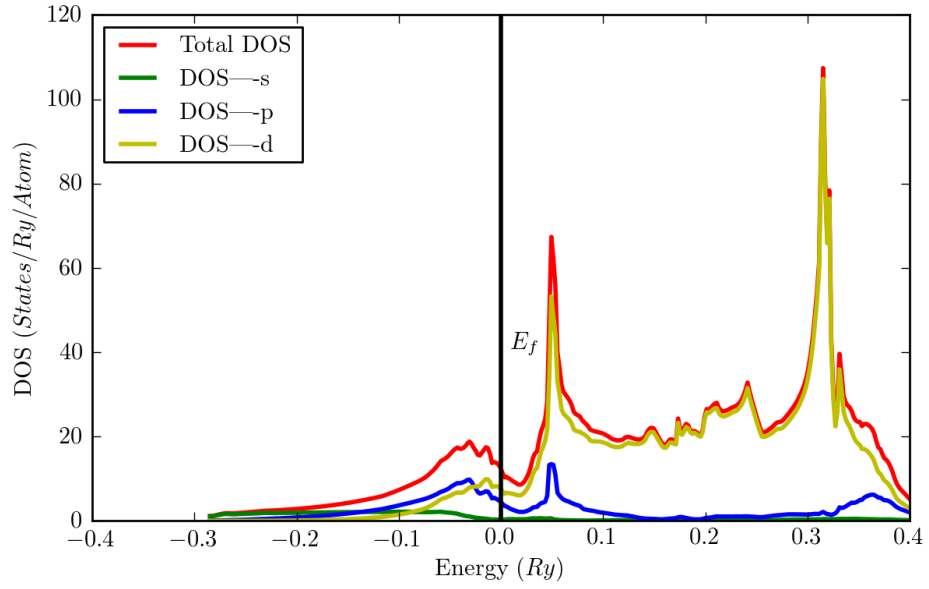


Figure 4.12: Density of States of Calcium calculated using NRL-TB parameters at $a = 10.20$ a.u.

Table 4.5: Comparison of LAPW-GGA and NRL-TB results of Density of States calculations of Calcium for various lattice constants.

Lattice constant	$N(E_f)$	s	p	d
<i>(states/Ry/atom)</i>				
LAPW-GGA				
10.20	10.63106	0.037770	0.672405	1.718880
10.40	12.16077	0.044565	0.698940	2.086815
10.48	12.68451	0.045795	0.699240	2.257380
10.60	13.63994	0.059955	0.725670	2.284650
10.80	14.70787	0.074400	0.716580	2.453505
NRL-TB				
10.20	16.28089	1.22555	3.43528	11.62005
10.40	16.95944	1.36299	3.75095	11.84550
10.48	17.34097	1.42019	3.88898	12.03180
10.60	17.90966	1.51078	4.10044	12.29843
10.80	19.01414	1.66063	4.48572	12.86779

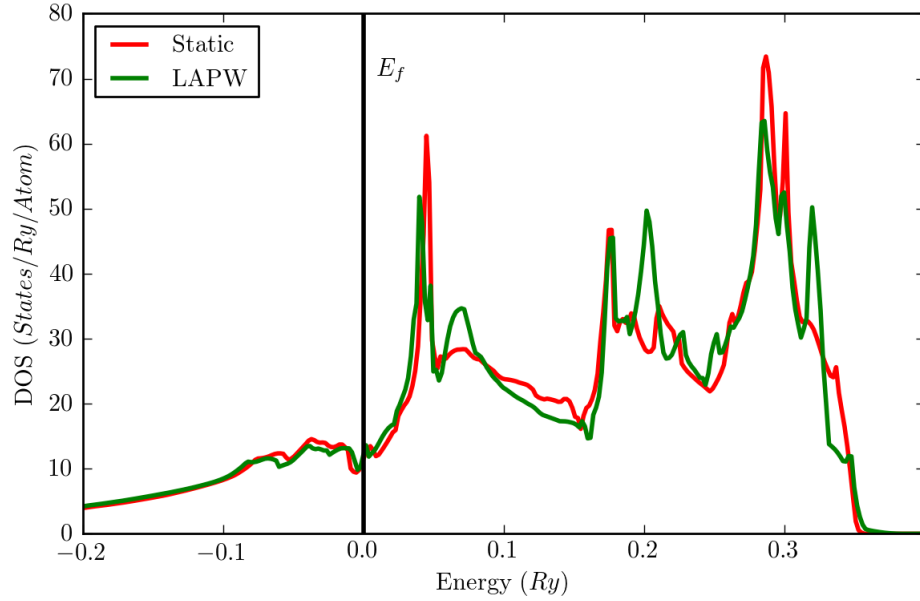


Figure 4.13: Density of States of Calcium calculated using LAPW-GGA and NRL-TB parameters at equilibrium lattice constant, $a = 10.4$ a.u.

4.8 Tight-Binding Molecular Dynamics

The TB parameters generated using the NRL-TB method is used with the TBMD package by Kirchhoff *et al.* [29] to determine thermodynamic properties. Using the TB parameters generated from the NRL-TB fit, TBMD has been performed on temperatures ranging from 100 – 1500 K for both fcc and bcc structures, and each temperature calculation has been run for 2000 steps. Figure 4.14 shows the equilibration for temperature of 300K.

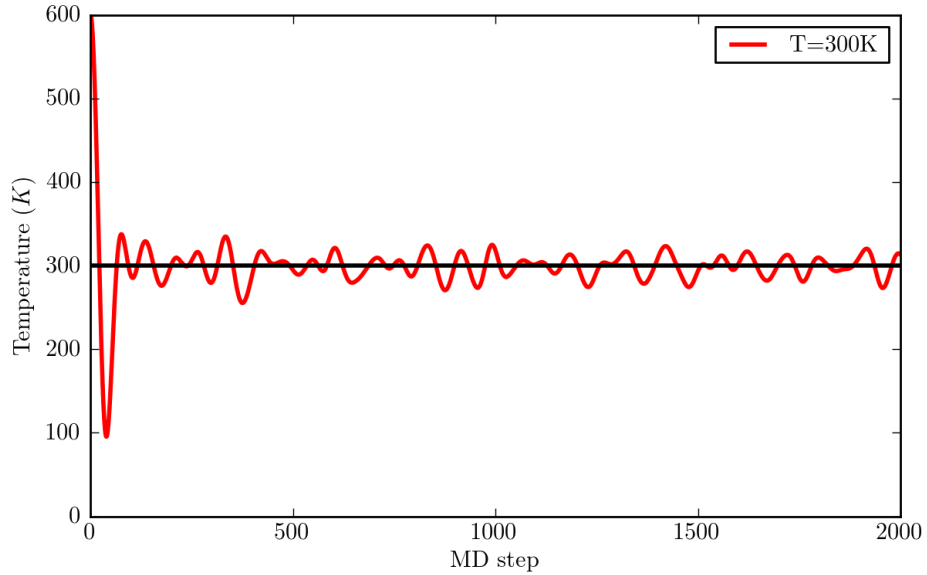


Figure 4.14: Equilibration of Calcium at $T = 300K$.

Melting point of Ca is 1112K and the results of the TBMD calculations are shown in Table 4.6. Unlike TBMD calculations in Sr, a repulsive potential has been used, to prevent unphysical behavior of the total energy at small volumes, as explained in Chapter 2, Section 2.16.

There is a phase change in Ca from fcc to bcc around 721K [70]. Moriarty [71] has suggested that transition temperature for Ca under zero pressure is 555K using hybridization and 245K without it, also when the crystal is compressed to 90%, the values

are 160K and 740K respectively. Olijnyk et al. [42] have been successful in performing MD simulations on 108 cubic super-cells. Sheng et al. [36] have used EAM potentials to calculate the melting temperature of Ca to be 980K.

Table 4.6: Results of TBMD on fcc structures of Calcium.

Target Temperature (K)	Equilibration Temperature (K)	
	bcc structure	fcc structure
100	106.81	93.57
200	205.04	193.51
300	313.17	303.71
400	418.00	388.17
500	516.16	499.84
600	610.58	586.02
700	717.47	718.54
800	832.07	843.05
900	941.27	909.49
1000	1105.68	1049.29
1100	1123.77	1161.97
1200	1269.29	1338.31

4.9 Mean Square Displacement

We have used the atomic positions generated by the MD simulations performed for several temperatures at the corresponding experimental lattice constants to compute the atomic MSD, which is an indication of atomic diffusivity, i.e., vibration of atoms with temperature over a time interval. It is an average of atomic positions, which are generated by TBMD over all atoms and time steps.

The MSD for each temperature is calculated in atomic units and is shown in Fig. 4.15. The MSD value is key in calculating the Debye-Waller factor. Comparisons with other calculations are also shown in Fig. 4.15.

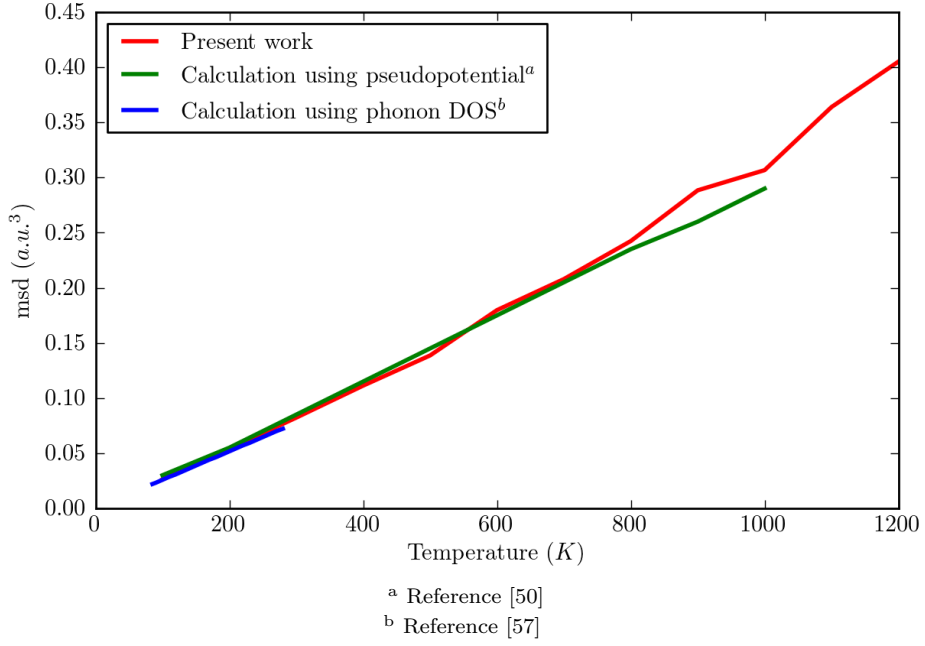


Figure 4.15: Mean square displacement for Calcium.

4.10 Vacancy Formation Energy

The VFE for Ca has been tested using a relaxed super-cell method with conjugate gradient approximation, in which the energy of a cell with a complete lattice is compared to a lattice in which one atom has been removed. The VFE indicates the stability of the structure due to the loss of an atom; a positive value means that the structure is more stable in the full lattice configuration.

Using the NRL-TB parameters, the VFE has been calculated to be 0.66 eV. Calculations using EAM potential [36] has predicted it to be as 0.95 eV. Manninen et al. [72] have calculated a range of VFE, depending on various methods used as 1.32 eV and 1.13 eV. The calculated values are corroborated by calculations using jellium model [58] as 0.69 eV.

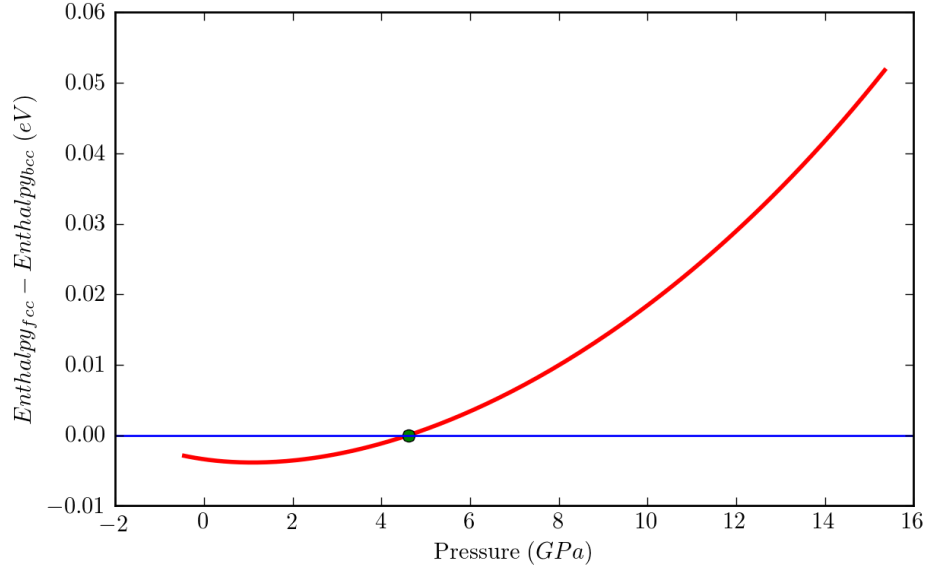


Figure 4.16: Difference in enthalpy for Calcium plotted against pressure in GPa.

4.11 Enthalpy

Enthalpy has been calculated for both fcc and bcc structures and the difference between enthalpies for fcc and bcc was plotted with respect to pressure in GPa as shown Fig. 4.16. An intersection with the zero difference line is found at 4.6 GPa at a volume of 232 Bohr^3 . This intersection indicates a phase change, and is much farther away from the 19.5 GPa transition pressure (at room temperature) predicted by experiment [42], but the calculated value is close to the 10.00 GPa calculations performed using first principles by Qiu et al. [73]. Animalu [70] has used pseudopotential to calculate a phase change at approximately 6.00 GPa, which is closer the calculated value of 4.6 GPa. Other calculations using FP LAPW [40] predict that this transition occurs from 0.9 GPa. These varied results, shown in Table 4.7, can be attributed to the fact that Ca is an extremely soft material and hence, its transition pressure is hard to predict.

Table 4.7: Transition pressures of Calcium from fcc to bcc structure.

	Transition pressure
	(<i>GPa</i>)
This work	4.6
Experiment ^a	19.5
First principles ^b	10.0
FP LAPW ^c	0.9
Pseudopotential ^d	6.0

^aReference [42]

^bReference [73]

^cReference [40]

^dReference [70]

4.12 Phonon Frequencies

We have used the NRL-TB parameters listed in Appendix A.2 to calculate phonon frequencies at high symmetry q-points using the frozen phonon approximation method. Table 4.8 lists the phonon frequencies in THz, calculated at experiment equilibrium of 10.48 Bohr, which are in good agreement with experiment [67] and other calculations using EAM potential [36].

We have also calculated the phonon frequencies at lattice constants varying from 10.2 – 10.8 Bohr. As pressure increases, i.e., lattice constant decreases, the frequencies show an upward trend as indicated in Fig. 4.17. The values of the phonon frequencies in THz are tabulated in Table 4.9.

Table 4.8: Phonon frequencies of Calcium at equilibrium fcc lattice constant in THz comparison with experiment and other calculated results.

	This work	Expt ^a	Pseudopotential ^b	First principles ^c	Expt ^d	EAM ^e
	(THz)					
X_3	3.45	4.52	4.80	5.20	5.00	4.59
X_5	3.12	3.63	3.50	3.80	3.50	3.52
L_2	4.26	4.61	4.70	4.90	4.80	4.46
L_3	2.17	2.36	2.30	2.30	2.30	2.32
W_2	2.62	3.66				
W_5	3.20	4.61				
Δ_1	3.17	3.66	3.20	3.50	3.80	
Δ_5	2.55	2.36	2.50	2.70	2.10	
Σ_1	3.86		3.50	4.00	3.00	3.87
Σ_2	2.18		2.10	2.10	2.10	3.11
Σ_3	4.30		4.00	4.50	4.00	4.27

^aReference [67]

^bReference [50]

^cReference [74]

^dReference [68]

^eReference [36]

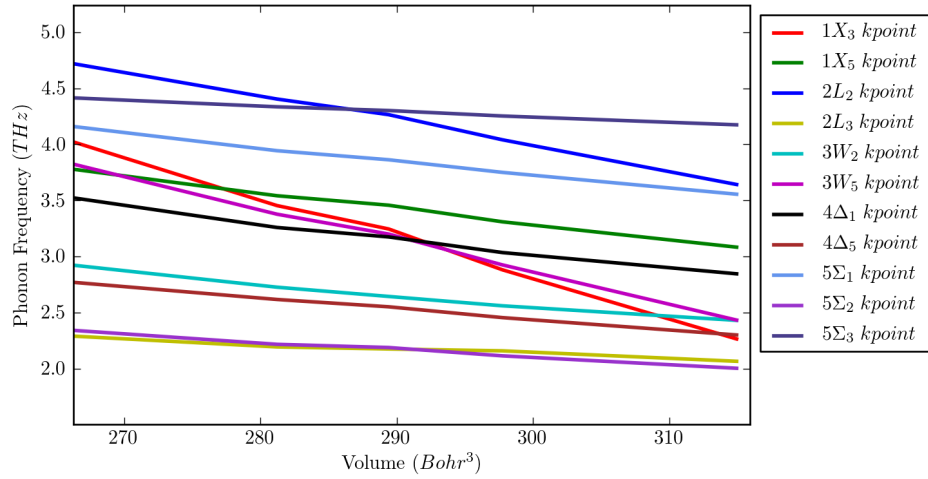


Figure 4.17: Variation of phonon frequencies of Calcium with respect to lattice constant.

Table 4.9: Variations of phonon frequencies of fcc structure of Calcium with respect to lattice constant.

Lattice Constant (<i>Bohr</i>)	10.2	10.4	10.48	10.6	10.8
k-points	(THz)				
X_3	3.79	3.54	3.45	3.31	3.08
X_5	4.06	3.45	3.24	2.88	2.26
L_2	4.74	4.40	4.26	4.04	3.64
L_3	2.30	2.19	2.17	2.15	2.06
W_2	2.93	2.73	2.64	2.56	2.43
W_5	3.85	3.37	3.20	2.93	2.43
Δ_1	3.54	3.25	3.17	3.04	2.84
Δ_5	2.78	2.61	2.55	2.46	2.30
Σ_1	4.17	3.94	3.86	3.75	3.55
Σ_2	2.35	2.21	2.18	2.11	2.00
Σ_3	4.42	4.33	4.30	4.25	4.17

4.13 Summary

In conclusion, using the NRL-TB method, two sets of transferable TB parameters for Ca has been successfully generated. The first set successfully predicts the total energies of structures that were not included in the fit. Also, mechanical properties like elastic constants and bulk modulus provide a good agreement with experiment. Large calculations including TBMD, MSD and VFE have been performed with much smaller computational time than with first principles. Enthalpy and phonon frequencies are a good estimate, using this set of TB parameters. The second set of TB parameters predict accurately the energy bands, DOS, and electronic specific heat coefficient.

Chapter 5: Alkali Metal: Rubidium

5.1 Rubidium

Rubidium (Rb) is an alkali metal, having only one electron in its outermost orbit. It is highly reactive, and oxidizes very rapidly. For this reason, it is very hard to accurately model it in solid form. The Naval Research Laboratory (NRL) group has not given successful Tight-Binding (TB) parametrizations for the alkali metals. This is partly because of their softness, and also due to the fact that Density Functional Theory (DFT) gives total energies for face centered cubic (fcc), body centered cubic (bcc), and hexagonal close packed (hcp), which are extremely close to each other. In this work, good TB Hamiltonian for one alkali metal, i.e., Rb, has been successfully obtained.

Compared to transition metals, heavy alkalis such as Rb have greater nearest neighbor interactions as predicted by Song et al. [75] and hence, contribute larger binding energies. This leads to misleading results when using computational predictive methods that work well with transition metals. Due to these factors, even though Song et al. [75] have modeled many bcc metals using discrete variational clusters, however, Rb has been left out. Other calculations of alkali metals using Augmented Plane Wave (APW) and Hartree-Fock have also ignored Rb as Dagens and Perrot calculations [76]. The authors of [77] have applied Random Phase Approximation (RPA) and DFT on various alkali, alkaline earth, and transition metals, however, their results for alkali metals, in particular Rb, showed the most variance. DFT calculations have been performed by the authors of [78] on heavy alkali metals focusing more on Potassium (K), and correctly predicting ground state of Rb to be bcc. However, an *ab initio* pseudopotential plane wave method using the local-density approximation by Li et al. [79] shows incorrectly fcc as stable state. APW and pseudopotential calculations of alkali metals, presented

by Allen et al. [80], do include Rb, but do not present any electronic properties other than Fermi surface energies, electron-phonon interactions and resistivity. Similar to calculations in this study, Ahuja et al. [81] have used a full-potential linear muffin-tin orbital method together with both the Local Density Approximation (LDA) and the Generalized Gradient Approximation (GGA) of Perdew and Wang (PW91). They have concluded that GGA works best with heavy alkali metals like Rb and Cesium (Cs), however, they do not present any other static or dynamic properties other than lattice constants and total energies.

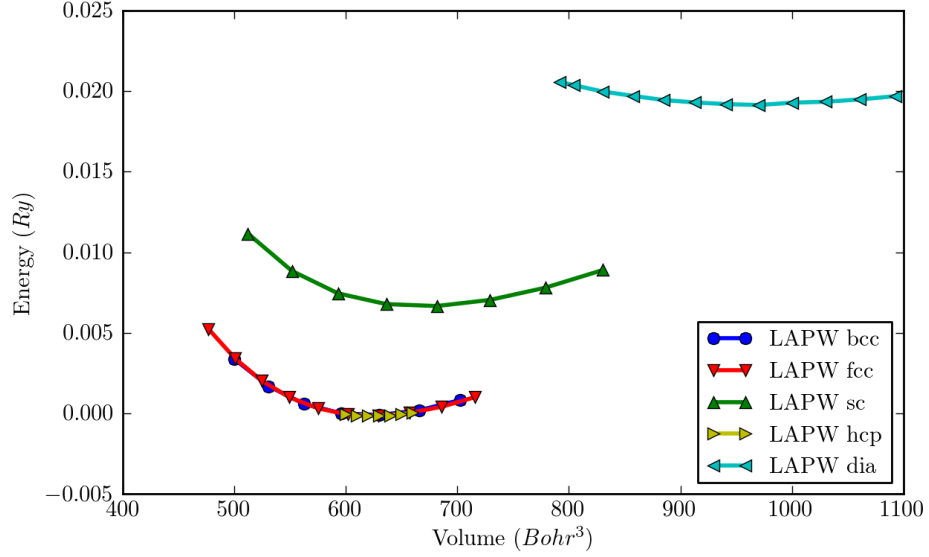


Figure 5.1: Total energies of bcc, fcc, sc, hcp, and dia structures of Rubidium generated using LAPW-GGA.

In ground state, i.e., at room temperature and normal pressure, Rb is bcc, however, with very small change in pressure, around 7.0 GPa, it transforms to fcc as calculated by Katzke et al. [82]. This transition has also been documented by Schwarz [83] and by Takemura et al. [84]. These low transition pressures observed in heavy alkali metals like K, Rb and Cs, can be attributed to pressure induced s-d transitions. Also, Katzke et al. [82] have shown more phase transitions of Rb at pressures of 13, 17, 19 and 48

GPa. McMahan [85] has shown that $s \rightarrow d$ transitions are caused by change in pressure. These phase sequences are interpreted as reflecting the hybridization process of the s- and d-wave functions, which induces a deformation of the atomic shells. Also, Rb has a very low melting temperature of 312K cited in Kittel [25] and boiling temperature of 961K.

This Chapter describes the results of Linear Augmented Plane Wave (LAPW)-GGA inputs to the NRL-TB fit, which gives a set of 97 TB parameters, which are then used to predict total energies for the following lattice structures: bcc, fcc, simple cubic (sc), hcp, and diamond (dia). Using these TB parameters, predictions are made on mechanical properties like elastic constants, for both bcc and fcc structures, band structure, Density of States (DOS), electronic specific heat coefficient, phonon frequencies, enthalpy, Molecular Dynamics (MD), Mean Square Displacement (MSD), and Vacancy Formation Energy (VFE).

5.2 LAPW-GGA

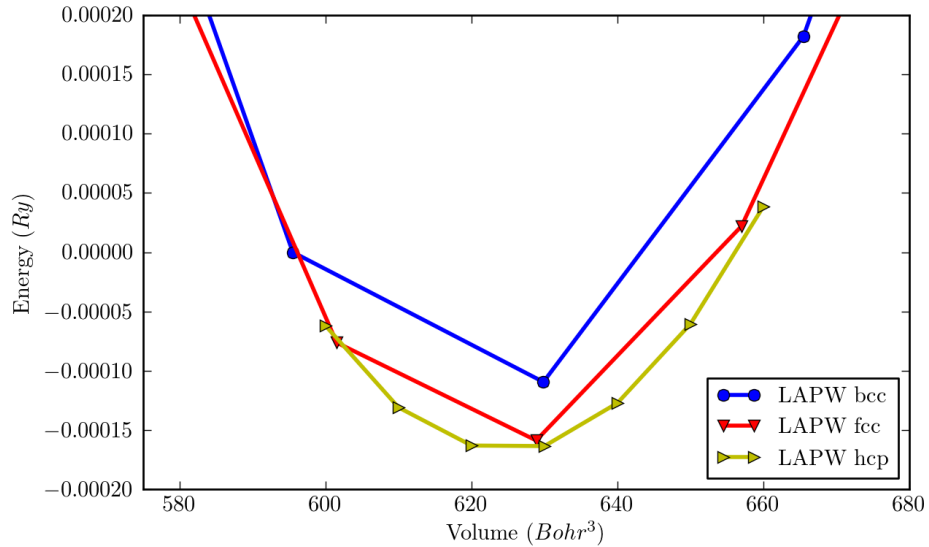


Figure 5.2: Zoomed version of Fig. 5.1 to show the near degeneracy of bcc, fcc, and hcp structures of Rubidium near equilibrium.

We have initially performed LAPW-GGA calculations to generate total energies for only fcc, bcc, and sc, which are fitted using the TB code. However, the TB parameters generated from this fit have shown in static, hcp as the ground state structure instead of bcc. Hence, LAPW-GGA inputs are generated for hcp and also dia, which still showed hcp as the equilibrium structure. This is shown in Fig. 5.1. Though some calculations have been able to correctly predict the ground state of Rb to be bcc, as March et al. [78], some others like those presented by Li et al. [79] have reached the same conclusion as ours. This can be attributed to the fact that Rb undergoes a phase change at a very small pressure of 7.0 GPa. Near equilibrium, energies of bcc, fcc, and hcp are nearly degenerate as shown in Fig. 5.2, and these energies are input to NRL-TB as-is. As it has been shown in the following sections, other than incorrectly predicting ground state, static and dynamic properties predicted are in good agreement with experiment and other calculations.

Table 5.1: Comparisons of Rubidium’s lattice constant and bulk modulus with experiment and other computational results.

	Lattice Constant (<i>Bohr</i>)	Bulk Modulus (<i>GPa</i>)
Present work LAPW-GGA input	10.748	2.70
Experiment ^a	10.559	2.50
Experiment ^b	10.554	3.10
Pseudopotentials ^c	10.599	2.56
Pseudopotentials ^d	10.554	2.47
Pseudopotentials ^e	9.8260	3.90
Pseudopotentials ^f	10.599	2.78

^aReference [45]

^bReference [25]

^cReference [86]

^dReference [87]

^eReference [88]

^fReference [89]

For fcc, energies were generated as a function of lattice constant and are in the range of 12.40 – 14.20 *Bohr*, for bcc 10.0 – 12.20 *Bohr*, for sc 8.00 – 9.40 *Bohr*. For hcp,

energies are generated as a function of volume of 610 to 650 $Bohr^3$ for c/a ratios of 1.50 to 1.75. The lattice with $c/a = 1.65$ is found to have the ground state among hcp, and these values were used as input to TB. Lattice constants are varied from 18.6 to 20.6 $Bohr$ for the dia lattice structure.

The lattice constant is predicted to be 10.748 $Bohr$, which is 1.78% more than the experiment values as shown in Table 5.1. Dunn's [88] estimate at 9.826 $Bohr$ is by far the most variance. Calculations using pseudopotentials by Price et al. [87] agree most with the experimental values presented in [45] as well as in [25].

Also, the bulk modulus has been calculated as the second derivative of energy with respect to lattice constant. It is predicted to be 2.7 GPa, which is in good agreement with the experiment value cited in [45] than to experimental values in [25]. Among other calculated values using pseudopotentials, by Dunn [88] have shown most variance, and by Ho [89] have the least deviation.

5.3 Tight-Binding

Non-orthogonal TB parameters, listed in Appendix A.4, are generated to fit total energies of bcc, fcc, sc, hcp, and dia. The range of lattice constants for fcc is 11.40 – 15.30 $Bohr$, for bcc 9.28 – 12.90 $Bohr$, for sc 8.00 – 9.40 $Bohr$, and for dia it is 19.00 – 20.60 $Bohr$. For hcp, the volumes fitted are from 600 to 650 $Bohr^3$. The fit generated is in good agreement with the LAPW-GGA values as shown in Fig. 5.3. The total RMS error for the total energies is 0.001070 Ry and that of the bands averages around 0.0275 Ry.

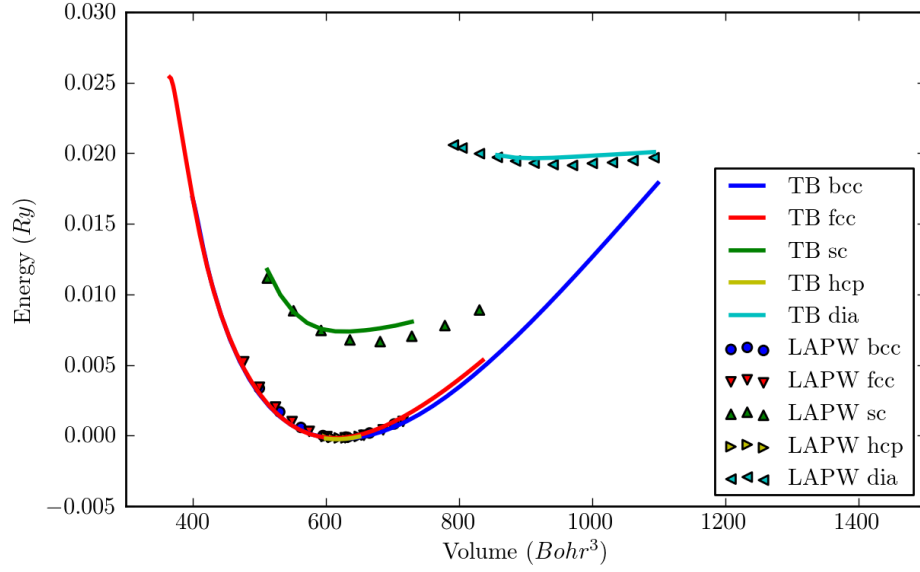


Figure 5.3: Total energies of bcc, fcc, sc, hcp, and dia structures of Rubidium from the NRL-TB fit in comparison with input energies generated using LAPW-GGA.

As expected, the ground state for Rb is not bcc. In fact, it replicates the input LAPW-GGA values, in which hcp is the lowest energy. However, unlike LAPW-GGA, the next highest energy is bcc and not fcc as shown in Fig. 5.5. For bcc, the lattice constant corresponding to the lowest energy is 10.750 Bohr , which is 1.8% greater than the experiment values of 10.559 Bohr .

The lowest lattice constant used in the fit for bcc is 9.28 Bohr , which is approximately 86% of the equilibrium lattice constant and hence, the TB parameters may be used as an input to the Tight-Binding Molecular Dynamics (TBMD) program. Unlike Sr and Ca, this proportion is a bit higher, however, like with Ca, the use of repulsive potential improves outcome of TBMD.

5.4 Total Energy

The TB parameters generated from the TB method are used to replicate the LAPW-GGA total energies for bcc, fcc, sc, hcp, and diamond structures as shown in Fig. 5.4.

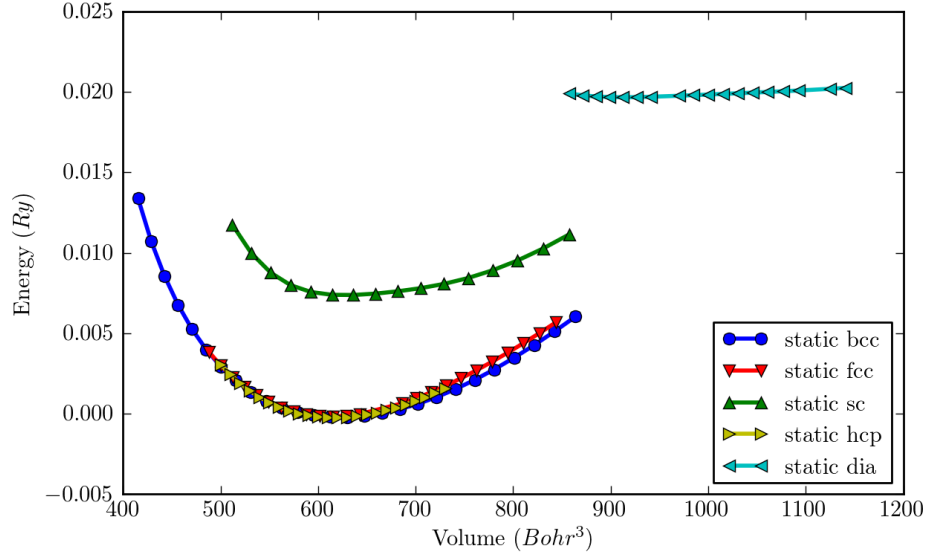


Figure 5.4: Total energies of bcc, fcc, sc, hcp, and dia structures of Rubidium generated using the NRL-TB parameters.

Fig. 5.5 shows a zoomed version of Fig. 5.4 to show and confirm that fcc is the ground state equilibrium structure.

Also, the energy of hcp lattice is plotted keeping the volume constant as the tetragonal strain has been varied. This tetragonal distortion is represented as a Bain path is shown in Fig. 5.7 and is explained in detail by Alippi et al. [51]. The Bain path shows a phase change from bcc to fcc when crystal is compressed as shown by Marcus et al. [37]. The path shows a minimum at c/a ratio of 1.65.

5.5 Elastic Constants

At equilibrium volume, elastic constants $C_{11} - C_{12}$ and C_{44} are found to have a value of 1.21 GPa and 1.46 GPa respectively. Both fcc and bcc elastic constants are shown in Fig. 5.8. Experiment value of $C_{11} - C_{12}$ in [45] is 0.52 GPa, which is 30% less than the calculated value 1.21 GPa, however, comparing C_{44} to experiment shows that the

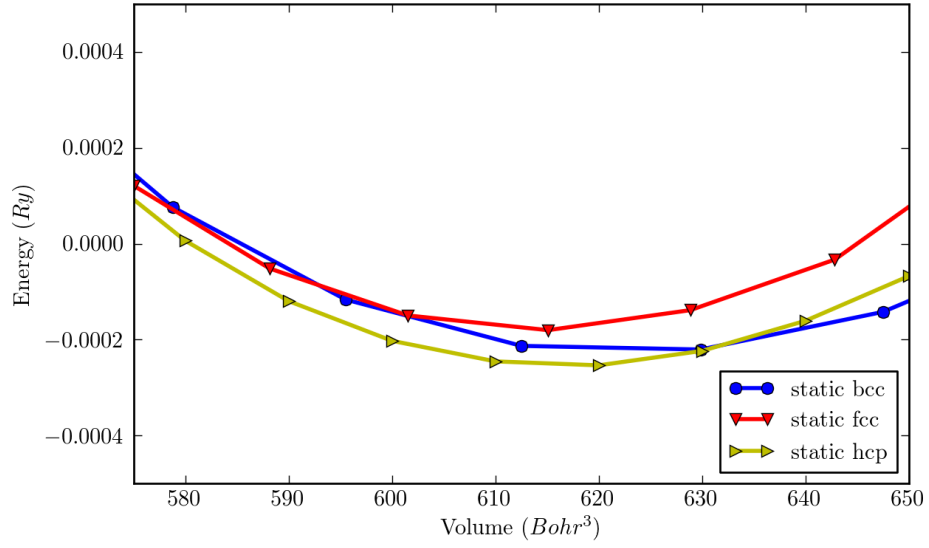


Figure 5.5: Zoomed view of Fig. 5.4 showing hcp structure of Rubidium has the lowest energy.

calculated value of 1.46 GPa is only 8% more than experiment. Unlike transition metals, these values are much smaller in magnitude. Even though previous calculations using LDA by Mehl et al. [2], have predicted values for Sr and Ca, this is the first time NRL-TB method has been successful for alkali metals. Computational values of $C_{11} - C_{12}$ presented by Sen et al. [90] and Li et al. [79] are in much agreement to the computed values. Calculations by Shapiro [91], and Ramamurthy et al. [92] agree with experiment better. Elastic constants for the fcc structure are also calculated, however, most other calculations ignore these elastic constants with an exception of those by Li et al. [79], whose values are in good agreement with that predicted using the NRL-TB parameters as shown in Table 5.2.

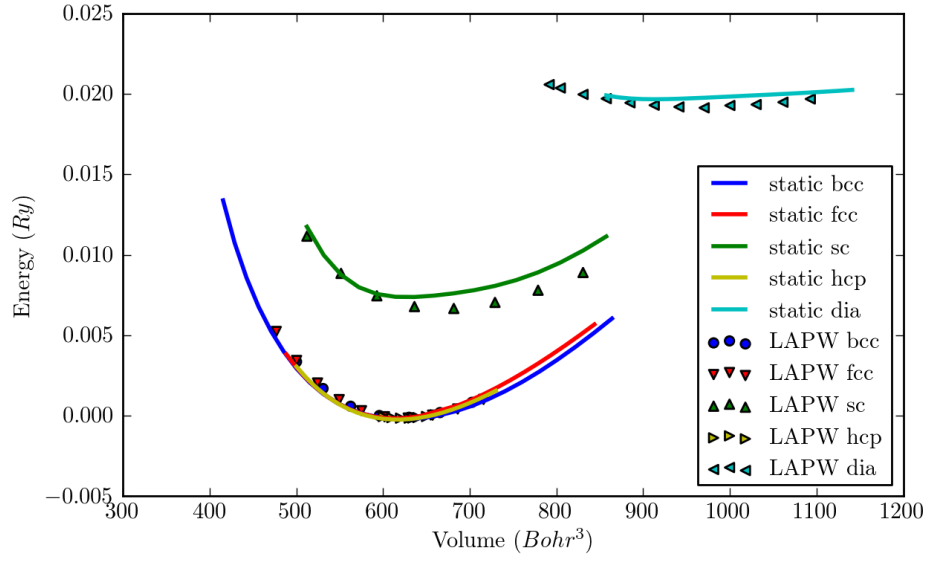


Figure 5.6: Total energies of bcc, fcc, sc, hcp, and dia structures of Rubidium obtained from NRL-TB parameters in comparison with energies of bcc, fcc, sc, hcp, and dia structures derived from LAPW-GGA.

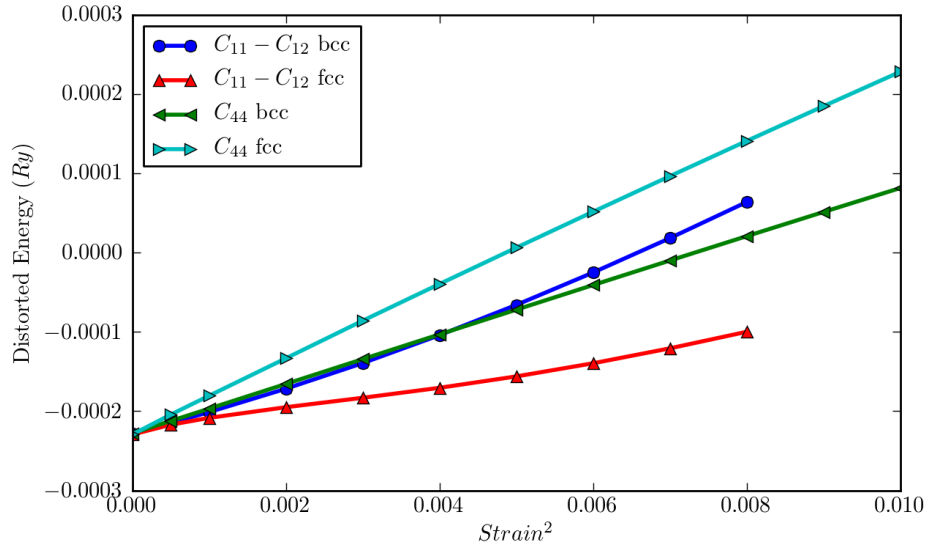


Figure 5.8: Linear relationship between distorted energy v. $strain^2$ of fcc and bcc structures of Rubidium. Slopes of these lines help to calculate elastic constants $C_{11} - C_{12}$ and C_{44} .

For both fcc and bcc, mechanical stability has been calculated over a range of different

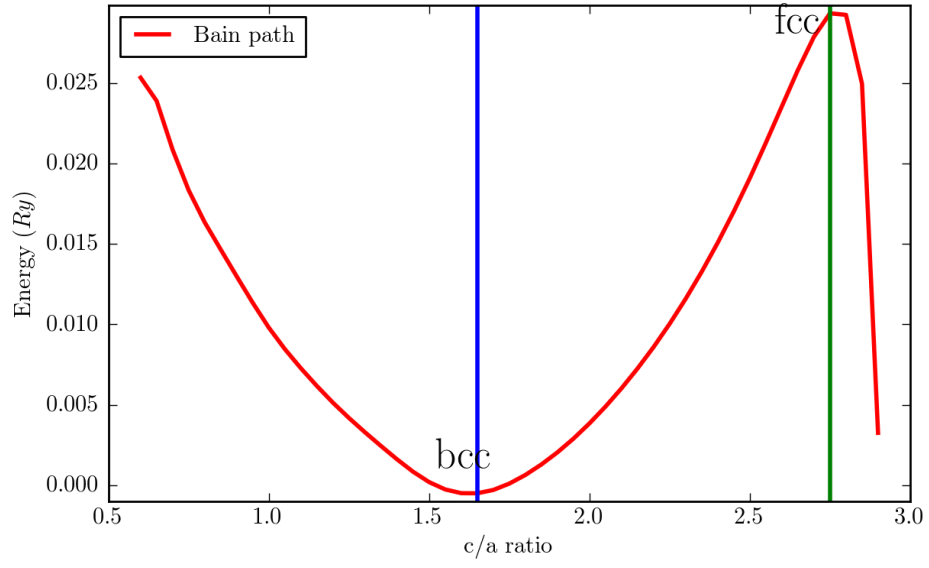


Figure 5.7: Bain path for Rubidium at experimental equilibrium volume of 621 $Bohr^3$.

volumes. The resultant graph in Fig. 5.9 shows an intersection between fcc and bcc values for C_{44} .

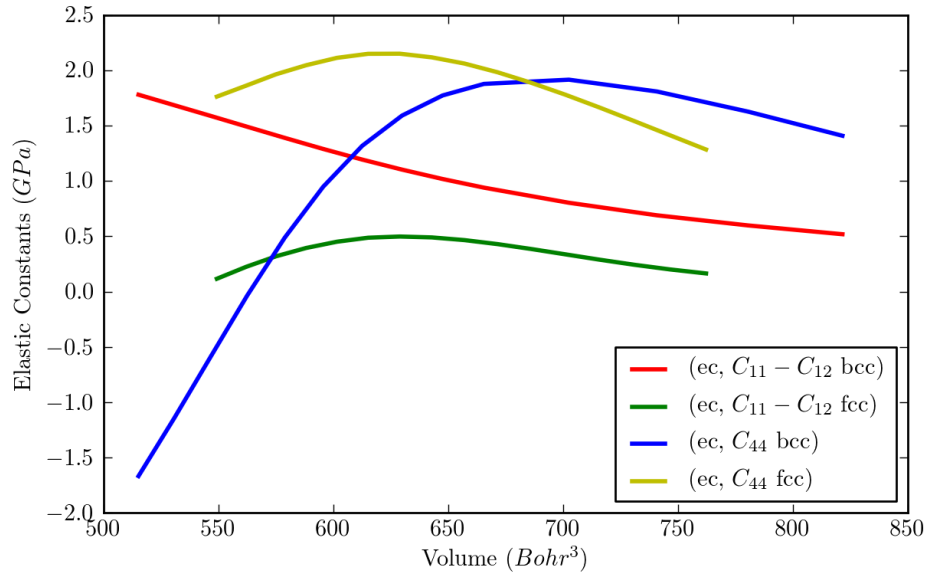


Figure 5.9: Change of elastic constants $C_{11} - C_{12}$ and C_{44} with respect to change in volume for various fcc and bcc lattices of Rubidium.

Table 5.2: Comparisons of Rubidium’s elastic constants of NRL-TB results with experiment and other computational results.

	bcc		fcc	
	$C_{11} - C_{12}$ (GPa)	C_{44} (GPa)	$C_{11} - C_{12}$ (GPa)	C_{44} (GPa)
Present work NRL-TB and GGA	1.21	1.46	0.49	2.15
Experiment ^a	0.52	1.60		
Moment trace method ^b	0.48	1.98		
General tensor force model ^c	0.05	1.86		
Reference handbook ^d	0.50	2.20		
Pseudopotential ^e	0.79	2.35		
PPW-LDA ^f	0.70	2.10	0.60	1.98

^aReference [45]

^bReference [91]

^cReference [92]

^dReference [93]

^eReference [90](indicates average value since a range was provided.)

^fReference [79]

5.6 Energy Bands

Like Ca, a second set of TB parameters have been generated, in which the root mean square (RMS) error for the band energies, and energy at only the equilibrium volume are minimized. This second set of TB parameters, listed in Appendix A.5, gives a better agreement of energy bands as well as DOS. Energy bands for bcc structure of Rb, calculated using LAPW-GGA, at ambient pressure are shown in Fig. 5.10. The energies have been shifted so that Fermi level E_f is zero. The band diagram confirms that Rb is a metal, since E_f crosses the bands between N and Γ k-points. Also, the electronic bands behave almost like free electrons below E_f . Energy bands generated using TB parameters are in good agreement with the energy bands generated by LAPW, but not as good as Sr and Ca.

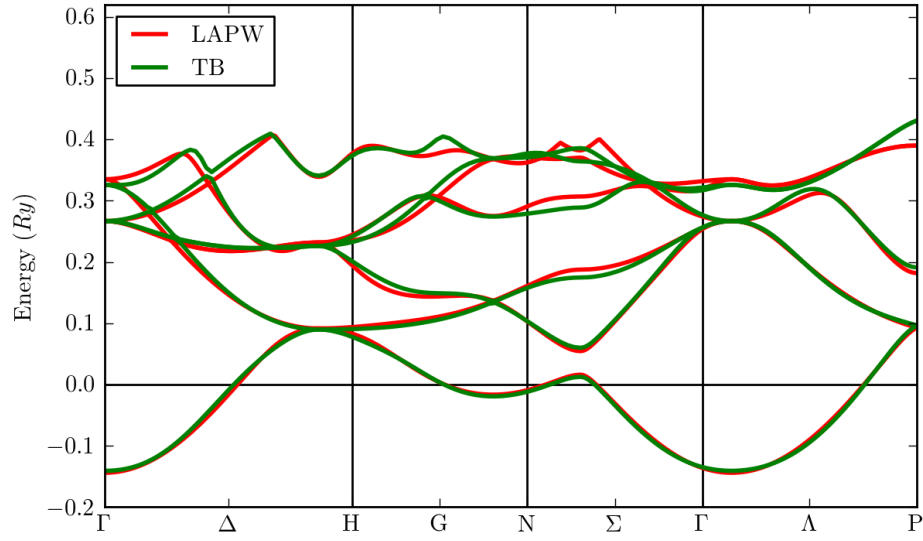


Figure 5.10: Comparison of energy bands of Rubidium using LAPW-GGA and NRL-TB parameters, at equilibrium lattice constant $a = 10.80$ a.u. All eigenvalues have been shifted so that the Fermi level is at zero.

5.7 Density of States

Table 5.3: Comparisons of LAPW and TB results of Density of State calculations for Rubidium.

	$N(E_f)$	s	p	d
	<i>(states/Ry/atom)</i>			
LAPW	16.21752	3.07403	1.37453	1.45680
TB	16.64918	8.86564	4.25186	3.53167

Unlike Sr and Ca, DOS for Rb has been calculated using 55 k-points corresponding to the bcc lattice, for both LAPW and TB. Fig. 5.11 shows the ambient pressure DOS of Rb, after shifting the eigenstate energies so that Fermi energy is zero. Also shown are the decomposed angular momentum that contribute to the total DOS. For low energies, the l-DOS are very small, and the remaining part is outside the MT spheres, because the bands at this position are free-electron like (plane waves). On the other hand, well

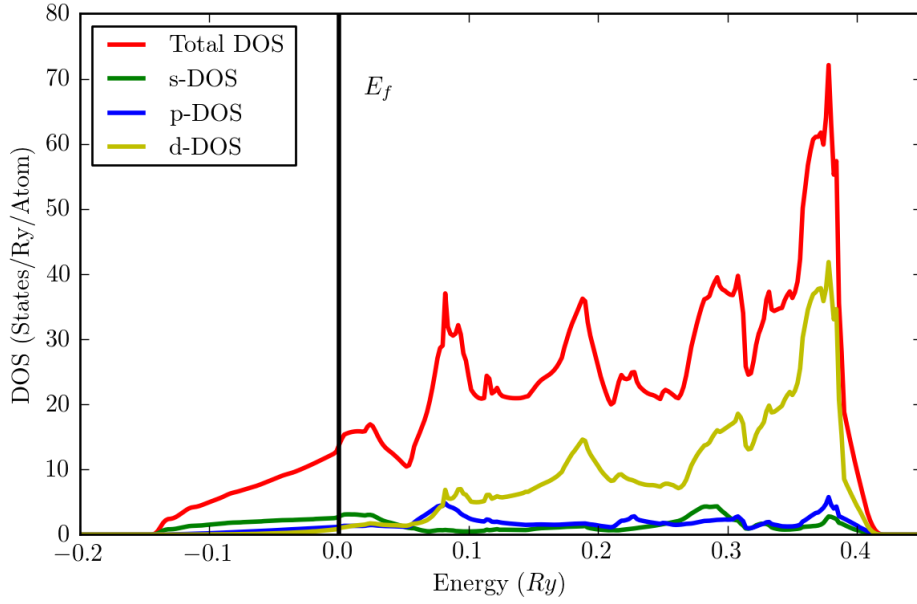


Figure 5.11: Density of States of Rubidium calculated using LAPW-GGA at equilibrium lattice constant $a = 10.80$ a.u. All eigenvalues are shifted so that the Fermi level is at zero.

above E_f the bands are almost exclusively d-like, which are localized inside the MTs and this is why the d-DOS is almost equal to the total DOS. TB parameters predicted DOS is as shown in Fig. 5.12. The exact values are shown in Table 5.3 along with decomposed angular momentum values. The value of Fermi energy from LAPW is close to other calculated values 0.136 and 0.135 Ry presented in [94] and [95] respectively.

We are able to calculate the electronic specific heat coefficient, using $N(E_f)$, to be 2.473 $mJ/(mol\ deg^2)$ using the Eq. (2.41). This value of γ is 2.5% smaller than the experimental value from Kittel [25] of 2.41 $mJ/(mol\ deg^2)$.

DOS determined by varying lattice constant from 10.00 – 11.20 *Bohr* have indicated that the Fermi energy has reduced with decreasing volume. This is shown in Table 5.4. In Fig. 5.13, DOS of Rb calculated using TB parameters at lattice constant of 10.6 *Bohr* is shown. In addition to the Fermi energy, the over all DOS are reduced under pressure.

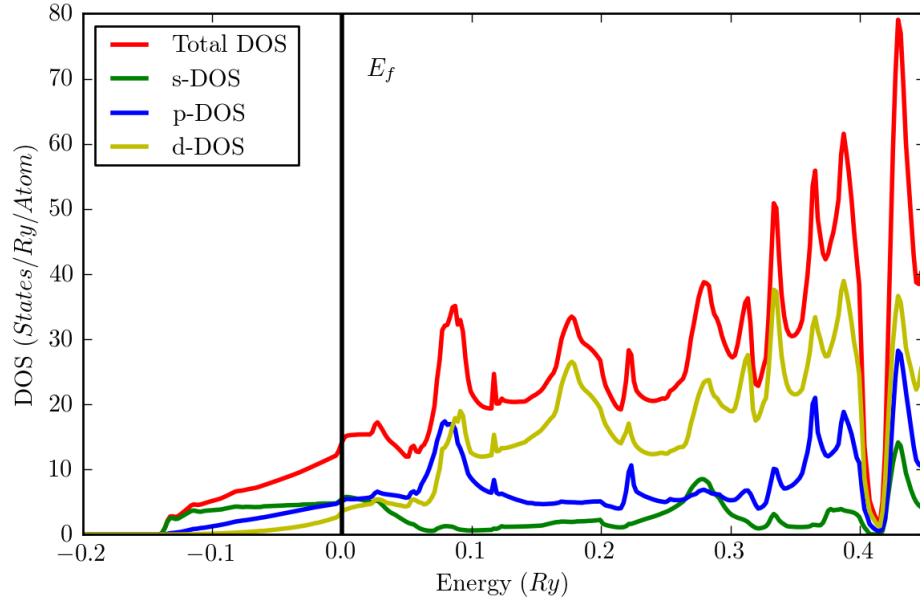


Figure 5.12: Density of States of Rubidium calculated using NRL-TB at equilibrium lattice constant $a = 10.80$ a.u. All eigenvalues are shifted so that the Fermi level is at zero.

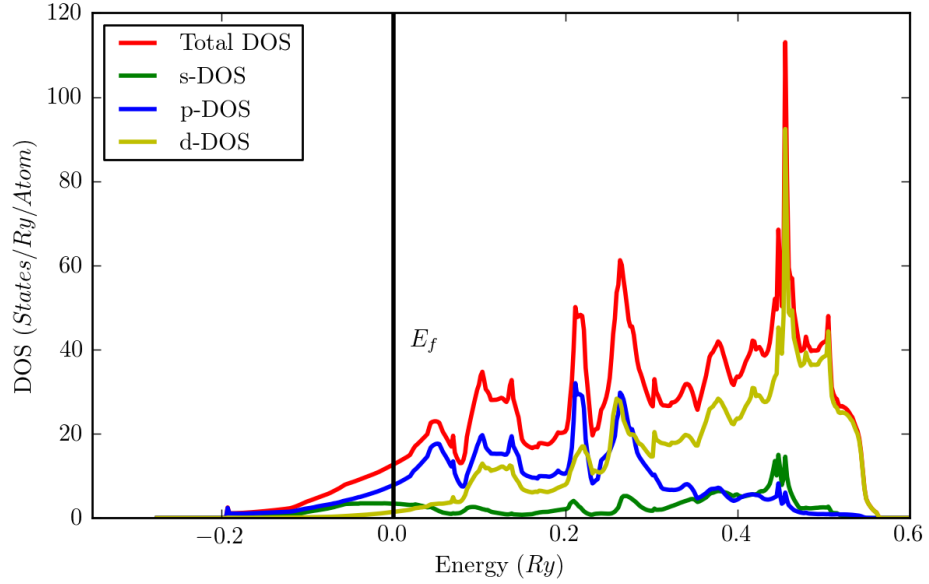


Figure 5.13: Density of States of Rubidium calculated using NRL-TB parameters at $a = 10.60$ a.u.

Table 5.4: Variation of LAPW and TB results of Density of States calculations for Rubidium with respect to change in volume.

Lattice constant	$N(E_f)$	s	p	d
	<i>(states/Ry/atom)</i>			
LAPW				
10.0	15.19334	3.24289	1.69725	2.08471
10.2	15.42966	3.18542	1.60078	1.88654
10.4	15.69265	3.13870	1.51070	1.71685
10.6	15.98577	3.10247	1.43261	1.56307
10.8	16.30544	3.08221	1.35717	1.42900
11.0	16.64996	3.07393	1.28582	1.31106
11.2	17.04979	3.14171	1.21992	1.22024
static				
10.0	11.99962	7.43146	3.38656	1.18161
10.2	13.14543	7.69289	3.56491	1.88761
10.4	14.62274	8.00563	3.88766	2.72945
10.6	15.97264	8.41185	4.15208	3.40871
10.8	16.80467	9.02942	4.27342	3.50182
11.0	17.23790	9.81926	4.26667	3.15196
11.2	17.59633	10.68312	4.21589	2.69735

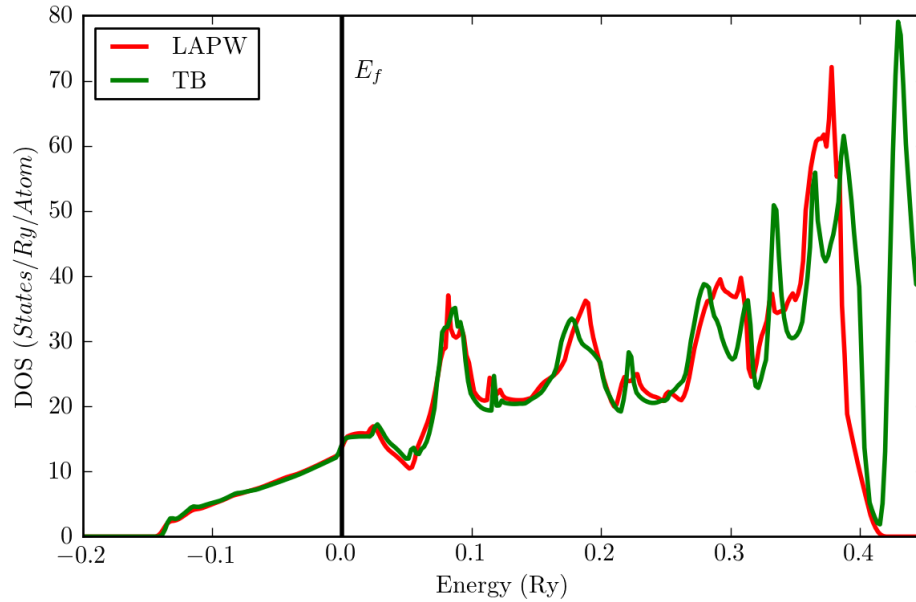


Figure 5.14: Density of States of Rubidium calculated using LAPW-GGA and NRL-TB parameters at equilibrium lattice constant $a = 10.8$ a.u. All eigenvalues are shifted so that the Fermi level is at zero.

A comparison of total DOS calculated using first principles LAPW-GGA and transferable TB parameters are as shown in Fig. 5.14. It has been observed that the peaks in both the LAPW-GGA DOS and the NRL-TB DOS occur in the same relative locations.

5.8 Tight-Binding Molecular Dynamics

Using the TB parameters generated from the fit, TBMD has been performed using repulsive potential, on temperatures ranging from 100 – 500 K for 7 x 7 x 7 bcc unit cells. Each temperature calculation has been run for 2000 steps. Figure 5.15 shows the equilibration for temperature of 100K.

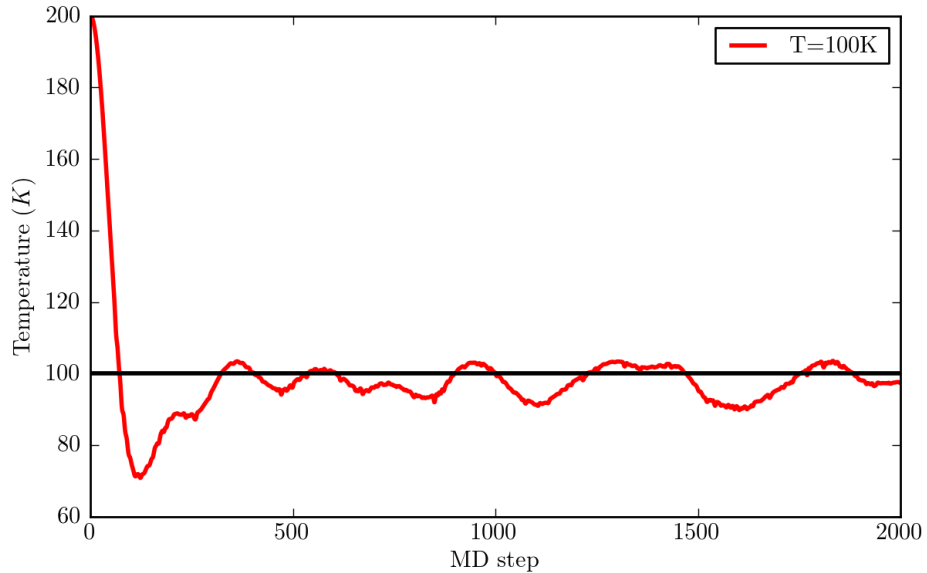


Figure 5.15: Equilibration of Rubidium at $T = 100K$.

The melting temperature of Rb is relatively very low at 312K, and MD was expected to break around that temperature. Molecular dynamics fails for a temperature run for 400K at 570K. Comparing to alkaline earth metals like, Sr and Ca, after 2000 steps, the temperature variance for Rb is much larger. Temperature values of each TBMD run is presented in Table 5.5.

MD calculations performed on solid alkali metals are rare, unlike calculations performed

on liquid alkalis. Other calculations using DFT and quantal hypernetted chain theory approximation, using 16,000 particles, have been performed on liquid alkali metals by Kambayashi et al. [96]. They have considered liquids to be an electron-ion mixture, and concluded that the melting point for Rb is 313 K. Similar MD calculations performed by Singh et al. [97], and verified the melting temperature of Rb.

Table 5.5: Results of TBMD on bcc and fcc structures of Rubidium.

Target Temperature (K)	Equilibration Temperature (K)	
	fcc structure	bcc structure
100	113.91	97.31
200	256.47	219.21
300	423.37	377.75

5.9 Mean Square Displacement

MSD is a characteristic of the vibrational properties of the elements. The atomic positions generated by the MD simulations performed for several temperatures at the corresponding experimental lattice constants have been used to compute the atomic MSD, which is an indication of atomic diffusivity, i.e., distance traveled by a particle over a time interval. It is an average of atomic positions, which are generated by TBMD over all atoms and time steps. The MSD for each temperature has been calculated in atomic units and is shown in Fig. 5.16, which is key in calculating the Debye-Waller factor.

Hübschle et al. [98] have used Green's function for the calculation of MSD for alkali metals, however, completely ignored Rb and Li. Shukla et al. [99] have performed MD calculations on 5 x 5 x 5 bcc unit cells, and the MSD calculated from the Debye-Waller factor is shown in Fig. 5.16.

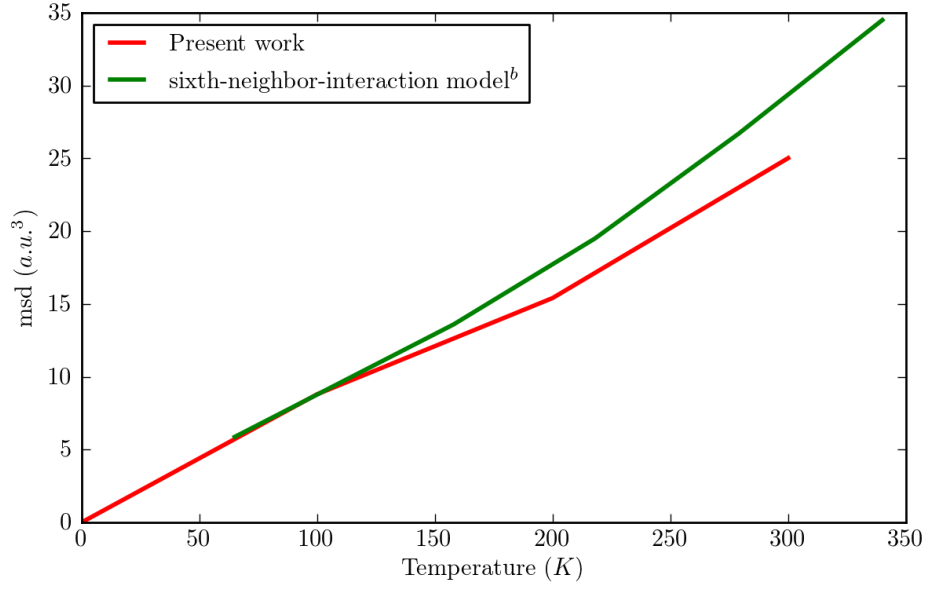


Figure 5.16: Mean square displacement of Rubidium.

^a Reference [57] ^b Reference [99]

5.10 Vacancy Formation Energy

The VFE for Rb has been tested via a relaxed super-cell method with conjugate gradient approximation, in which the energy of a cell with a complete lattice is compared to a lattice in which one atom has been removed. The VFE indicates the stability of the structure due to the loss of an atom; a positive value means that the structure is more stable in the full lattice configuration.

Using the NRL-TB parameters, the VFE has been calculated to be 0.17 eV. Since Rb is a very soft material, the VFE is hard to predict. This calculated value is corroborated by calculations using jellium model [58] as 0.27 eV. Manninen et al. [72] have calculated a range of VFE, depending on various methods used as 0.38 – 0.54 eV. Magaña [100] has also used pseudopotentials to calculate it to be 0.297 eV and Zhang et al. [101] has used Embedded Atom Method (EAM) to predict VFE as 0.342 eV.

5.11 Enthalpy

Enthalpy has been calculated for both fcc and bcc structures, and the difference between enthalpies has been plotted v. pressure in Fig. 5.17. An intersection has been observed between the enthalpies, and it is found at pressure of 1.37 GPa. This intersection indicates a phase change and is 80% less than the 7 GPa transition pressure (at room temperature) predicted by Katzke et al. [82] and is confirmed by calculations performed by Schwarz [83] and Takemura et al. [84]. However, when compared with transition metals, which have transitions pressures in triple digits, this variation is comparable.

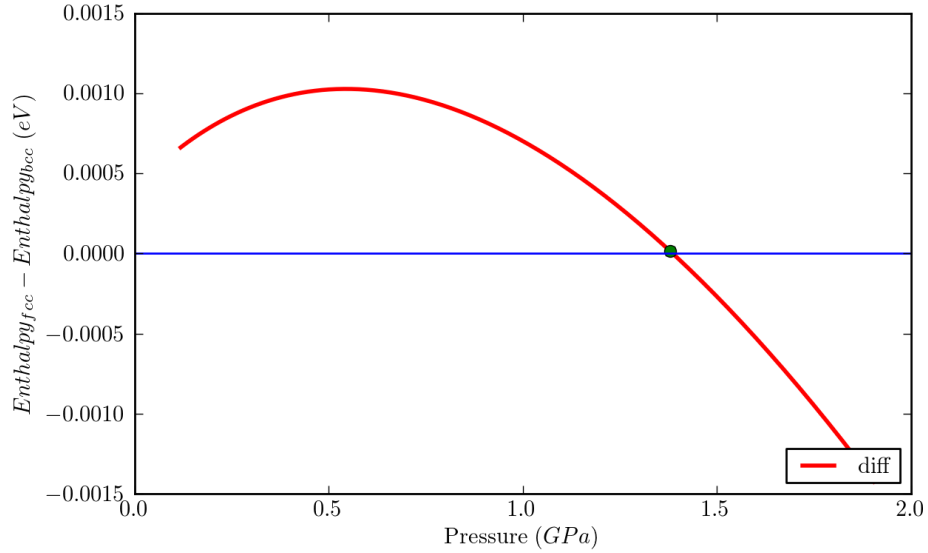


Figure 5.17: Difference in enthalpy for fcc and bcc structures of Rubidium v. pressure.

5.12 Phonon Frequencies

Using the frozen phonon approximation method, phonon frequencies for Rb have been calculated in THz, at high symmetry k-points, for bcc at experiment equilibrium of 10.75 *Bohr* as well as other lattice constants. Table 5.6 shows comparison of phonon frequencies with other computed values. The values for the H [100], N [110], and P [111] k-points are in good agreement with other calculated values. Of all the calculations

compared, phonon frequencies are in good agreement with those presented in [87] and [90], which have used pseudopotentials to study alkali metals.

Table 5.6: Phonon frequencies for Rubidium compared with other calculated results.

k-points	Our results	GTF ^a	Pseudopotential ^b	Non-central force ^c	OPW EIME ^d
	(THz)				
Δ_1	0.9653	1.10	1.00	0.90	1.10
Δ_5	0.7847	0.80	0.80	0.75	0.90
H	1.2214	1.26	1.25	1.30	1.30
N_2	0.8628	0.75	0.80	0.85	0.90
N_3	1.5235	1.00	1.30	1.45	1.45
N_4	0.2397	0.25	0.25	0.30	0.30
P	0.9923	1.10	1.10	1.20	1.10

^aReference [92]

^bReference [90]

^cReference [102]

^dReference [103]

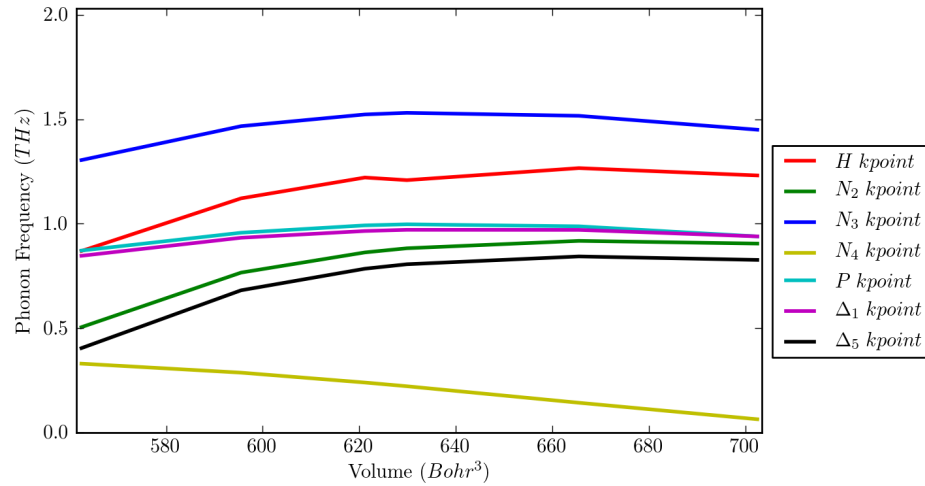


Figure 5.18: Variation of phonon frequencies of Rubidium with respect to pressure.

In addition to calculating phonon frequencies at equilibrium volume, the phonon fre-

quencies have also been calculated for each k-point by varying volumes from 560 to 700 $Bohr^3$. The calculated values are presented in Table 5.7. As pressure increases, the frequencies show a downward trend as indicated in Fig. 5.18, with the exception of N_4 k-point. This behavior is unlike the alkaline earth metals, which show an upward trend. However, when the crystal is allowed to expand, all frequencies of almost all k-points remain the same at equilibrium.

Table 5.7: Variations of phonon frequencies of Rubidium with respect to lattice constant.

Lattice Constant($Bohr$)	10.4	10.6	10.75	10.8	11.0	11.2
k-points	(THz)					
Δ_1	0.8467	0.9330	0.9653	0.9710	0.9707	0.9395
Δ_5	0.4045	0.6814	0.7847	0.8062	0.8435	0.8269
H	0.8696	1.1217	1.2214	1.2411	1.2665	1.2314
N_2	0.5050	0.7662	0.8628	0.8827	0.9180	0.9050
N_3	1.3051	1.4674	1.5235	1.5312	1.5170	1.4504
N_4	0.3302	0.2869	0.2397	0.2219	0.1429	0.0639
P	0.8716	0.9571	0.9923	0.9975	0.9878	0.9395

5.13 Summary

To reiterate, for Rb, the NRL-TB method has successfully generated two sets of transferable TB parameters. The first set favourably predict total energies of structures that were not included in the fit. Also, mechanical properties like elastic constants and bulk modulus provide a good congruence with experiment. Large calculations including TBMD, MSD and VFE have been performed with higher speed than with first principles. Enthalpy and phonon frequencies are a good estimate with respect to experiment, using this set of TB parameters. The second set of TB parameters predict accurately the energy bands, DOS, and electronic specific heat coefficient.

Chapter 6: Alkali Metal: Lithium

6.1 Lithium

The second alkali metal presented in this dissertation is Lithium (Li), which is highly reactive, flammable, and oxidizes very rapidly. It is the lightest metal with only three electrons per atom, and it is also the least dense metal. Hence, it displays complex behavior in some of its physical properties. It does not appear freely in nature except as part of compounds. For these reasons, it is very hard to accurately model it. There are no successful TB parametrizations for the alkali metals by the NRL group. This is partly because of their extreme softness, and also due to the fact that DFT gives total energies for fcc, bcc, and hcp which are extremely close to each other. In this work, some insights into applying this method to Li and the related challenges, have been presented.

At ambient conditions of temperature and pressure, the stable lattice structure of Li is bcc; however, change in temperature and pressure causes it to change into one of the following structures: hcp, fcc or 9R (a close-packed phase with a nine-layer stacking sequence). Harris et al. [104] have shown the resemblances between the bcc and 9R structures as in Fig. 6.1. The 9R structure is a distorted bcc structure in the (110) direction. The 9R structure has been shown to co-exist with bcc at really low temperatures of 70K, as studied by McCarthy et al. [105], using neutron diffraction experiments. This martensitic phase transformation has been confirmed by Smith [106] using a neutron elastic- and inelastic-scattering study. Stager et al. [107] have measured the pressure dependent phase transformation at 7 GPa, which has been confirmed by X-ray diffraction measurements performed by Olinger et al. [108]. Density functional calculations of alkali metal by March et al. [78] have ignored Li. Song et al. [75] have included Li in their study of bcc metals using first principles method, however, presented only total energies and DOS values. Dunn [88] has presented only lattice constant and bulk

modulus calculated using pseudopotential method.

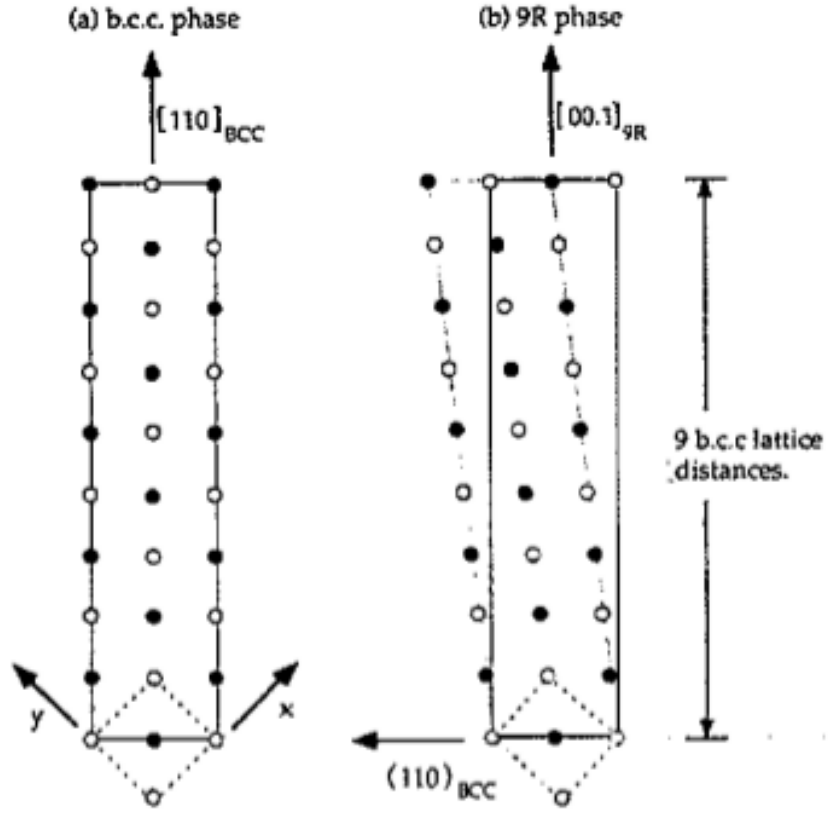


Figure 6.1: Resemblances between bcc and 9R structures ^a.

^aReference [104]

This chapter describes the results of LAPW-GGA inputs to the NRL-TB fit, which gives a set of 97 TB parameters, which are then used to predict total energies for the various lattice structures. Using these NRL-TB parameters, predictions are made on lattice constant, bulk modulus, band structure, DOS, electronic specific heat coefficient, and enthalpy. Also, provided is a discussion of the properties that are not in good agreement with experiment such as elastic constants and phonon frequencies .

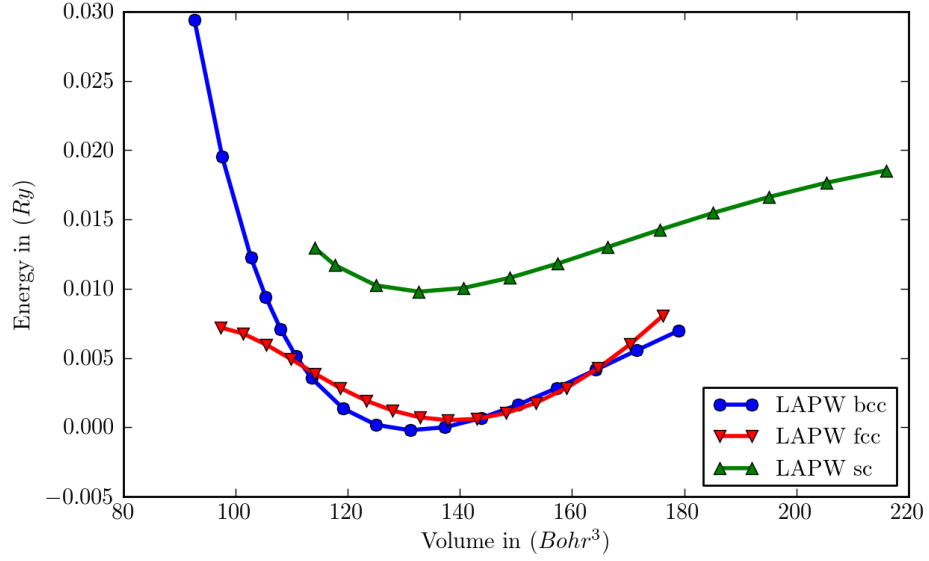


Figure 6.2: Total energies of Lithium for fcc, bcc, and sc structures generated using LAPW-GGA.

6.2 LAPW-GGA

We have initially performed LAPW-GGA calculations to generate total energies for only fcc, bcc, and sc, which are fitted using the TB code. However, the TB parameters generated from this fit have shown in static, hcp as the ground state structure instead of bcc. Some calculations have been able to correctly predict the ground state of Li to be bcc, as Ahuja et al. [81]. These energies are shown in Fig. 6.2. This can be attributed to the fact that Li undergoes a phase change at a very small pressure, which has been determined to be a wide range of 0.3 – 7.5 GPa. Near equilibrium, energies of bcc, fcc, and hcp are nearly degenerate, and these energies are input to NRL-TB as-is.

The lattice constant is predicted to be 6.401 Bohr, which is 3.46% smaller than the experiment values as shown in Table 6.1. Dunn’s [88] estimate at 6.134 Bohr is by far the most variance. Calculations using pseudopotentials by Rasky et al. [109] agree most with the experiment values presented in [45] as well as in [25].

Also, the bulk modulus has been calculated as the second derivative of energy with

Table 6.1: Comparisons of Lithium's lattice constant and bulk modulus with experiment and other computational results.

	Lattice Constant (<i>Bohr</i>)	Bulk Modulus (<i>GPa</i>)
Present work LAPW-GGA input	6.401	7.12
Experiment ^a	6.631	10.80
Discrete variational cluster method ^b	6.559	10.60
Pseudopotentials ^c	6.562	13.50
Pseudopotentials ^d	6.134	13.77

^aReference [45]

^bReference [75]

^cReference [109]

^dReference [88]

respect to lattice constant. It is predicted to be 7.12 GPa, which is in reasonable agreement with experimental values [45]. Values of bulk modulus calculated using pseudopotentials, by Dunn [88] and by Rasky et al. [109] are almost double the calculated value of 7.12 GPa. Song et al. [75] have calculated bulk modulus using a first principles discrete variational cluster method, and it is in good agreement with experiment.

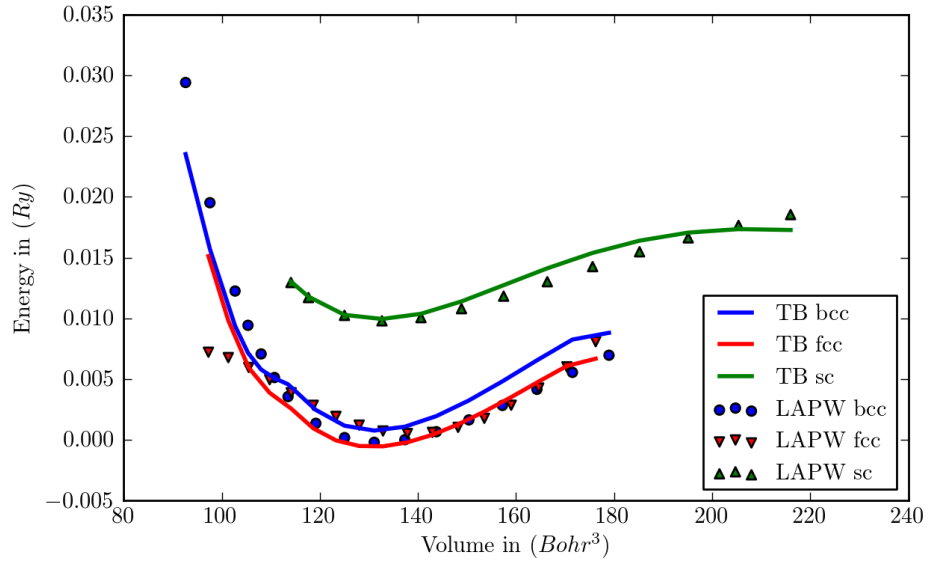


Figure 6.3: Total energies of fcc, bcc, and sc structures of Lithium obtained from NRL-TB in comparison with input values from LAPW-GGA.

6.3 Tight-Binding

Non-orthogonal TB parameters, listed in Appendix A.6, are generated to fit total energies of bcc, fcc, and sc. Unlike Sr, Ca, and Rb, the parameters are fitted only for the s and p bands and hence, the matrix to be diagonalized is 4×4 instead of 9×9 . The range of lattice constants for fcc is $7.30 - 8.90 \text{ Bohr}$, for bcc $5.70 - 7.10 \text{ Bohr}$, and for sc $5.00 - 6.00 \text{ Bohr}$. The fit generated is a close match with the LAPW-GGA values as shown in Fig. 6.3. The total RMS error for the total energies of Li is greater than that of Rb at 0.002018 Ry and that of the bands averages around 0.0275 Ry .

Unlike Rb, the TB-NRL fit corrects the ground state of Li to be bcc. For bcc, the lattice constant corresponding to the lowest energy is 6.4 Bohr same as the LAPW-GGA inputs.

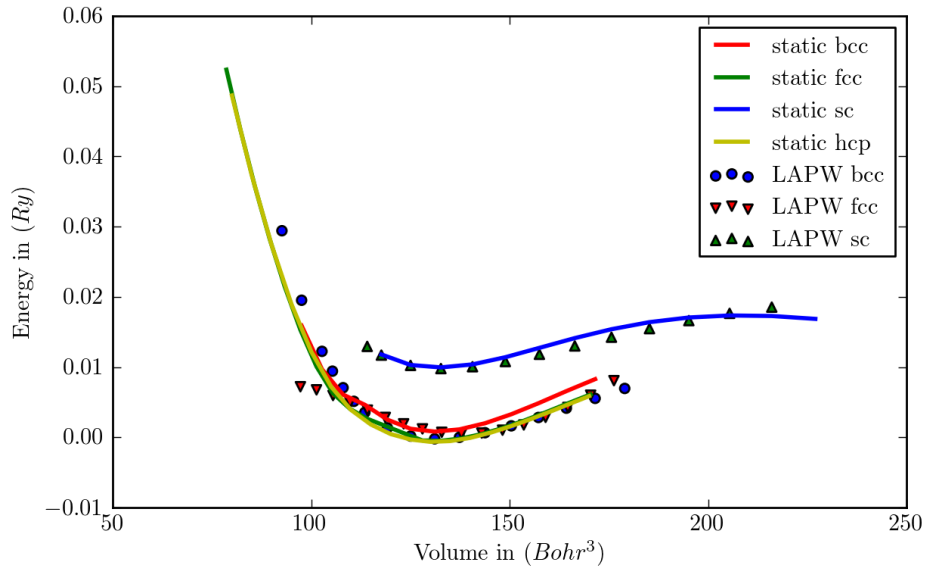


Figure 6.4: Total energies of fcc, bcc, sc, and hcp structures of Lithium generated using the NRL-TB parameters compared with input values of fcc, bcc, and sc energies generated using LAPW-GGA.

6.4 Total Energy

The TB parameters generated from the TB method are used to replicate the LAPW-GGA total energies for bcc, fcc, sc, and hcp as shown in Fig. 6.4. Fig. 6.5 shows a zoomed version of Fig. 6.4 to show that hcp is predicted as the ground state. This Hamiltonian has reproduced the LAPW results that were fitted, but was not capable in predicting the correct energy for the diamond lattice.

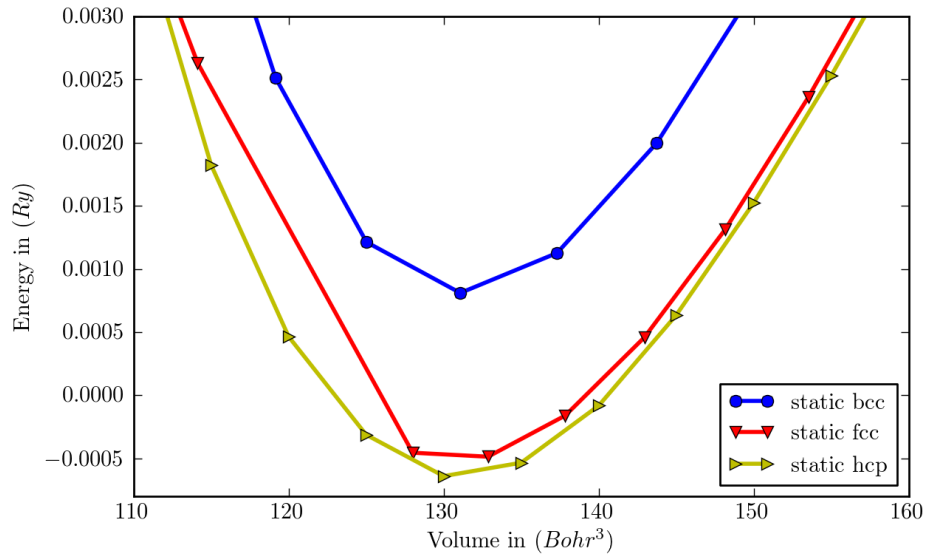


Figure 6.5: Zoomed view of Fig. 6.4 showing hcp structure of Lithium has the lowest energy.

6.5 Elastic constants

Unlike other elements in this study, the elastic constants $C_{11} - C_{12}$ and C_{44} are negative. This suggests that the bcc structure for Li is unstable, and this TB parametrization may favor the complicated 9R structure, which has not been considered in this study of Li.

6.6 Energy Bands

Like Rb and Ca, a second set of TB parameters for Li have been generated, in which the RMS error for the band energies and energy at only the equilibrium volume have been minimized. Also, in the calculation of this set of parameters, the d orbital is also included with s and p . This second set of TB parameters, listed in Appendix A.7, gives a better agreement of energy bands as well as DOS.

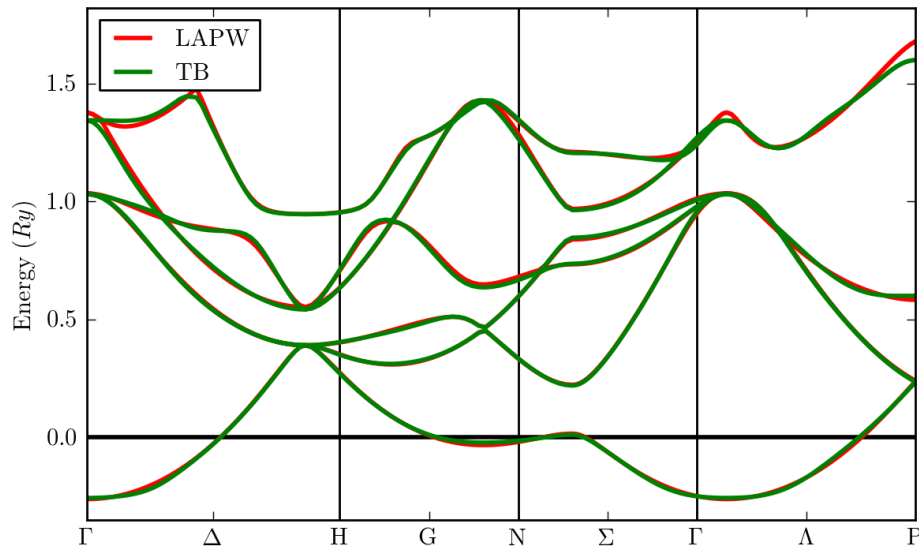


Figure 6.6: Comparison of energy bands of Lithium generated using LAPW-GGA and NRL-TB parameters, at equilibrium lattice constant $a = 6.60$ a.u. All eigenvalues have been shifted so that the Fermi level is at zero.

Energy bands for bcc structure of Li, calculated using LAPW-GGA, at ambient pressure are shown in Fig. 6.6. The energies have been shifted so that Fermi level E_f is zero. The band diagram confirms that Li is a metal, since E_f crosses the bands between N and Γ k-points. Also, the electronic bands behave almost like free electrons below E_f . Energy bands generated using TB parameters are in good agreement with the energy bands generated by LAPW, but not as good as Sr and Ca.

6.7 Density of States

Similar to the other bcc alkali metal in this study, DOS for Li has been calculated using 55 k-points, for both LAPW and TB. Fig. 6.7 shows the ambient pressure DOS of Li, after shifting the eigenstate energies so that Fermi energy is zero. Also, shown are the decomposed angular momentum values that contribute to the total DOS. For low energies, the l-DOS are very small and the remaining part is outside the MT spheres, because the bands at that position are free-electron like (plane waves). Fig. 6.8 shows the DOS for Li generated using the NRL-TB parameters. The exact values are shown in Table 6.2 along with decomposed angular momentum values.

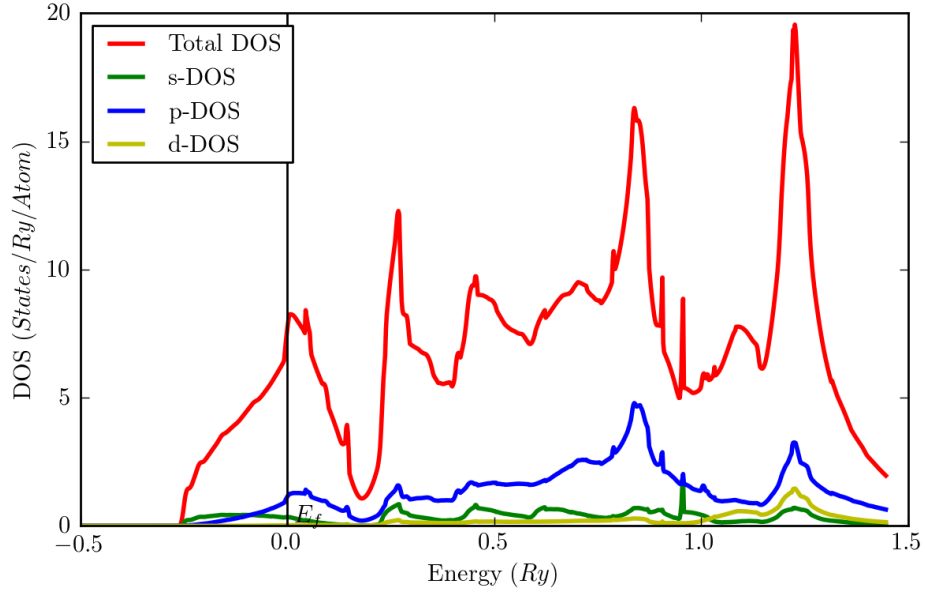


Figure 6.7: Density of States of Lithium calculated using LAPW-GGA at equilibrium lattice constant $a = 6.60$ a.u. All eigenvalues are shifted so that the Fermi level is at zero.

A comparison of total DOS calculated using first principles LAPW-GGA and transferable TB parameters are shown in Fig. 6.9. It is observed that the peaks in both the LAPW-GGA DOS and the NRL-TB DOS occur in the same relative locations.

Table 6.2: Comparisons of LAPW and TB results of Density of State calculations for Lithium.

	$N(E_f)$	s	p	d
	$(states/Ry/atom)$			
LAPW	10.0537	0.49338	1.43554	0.0317
TB	7.27207	1.50512	5.76694	0.0000

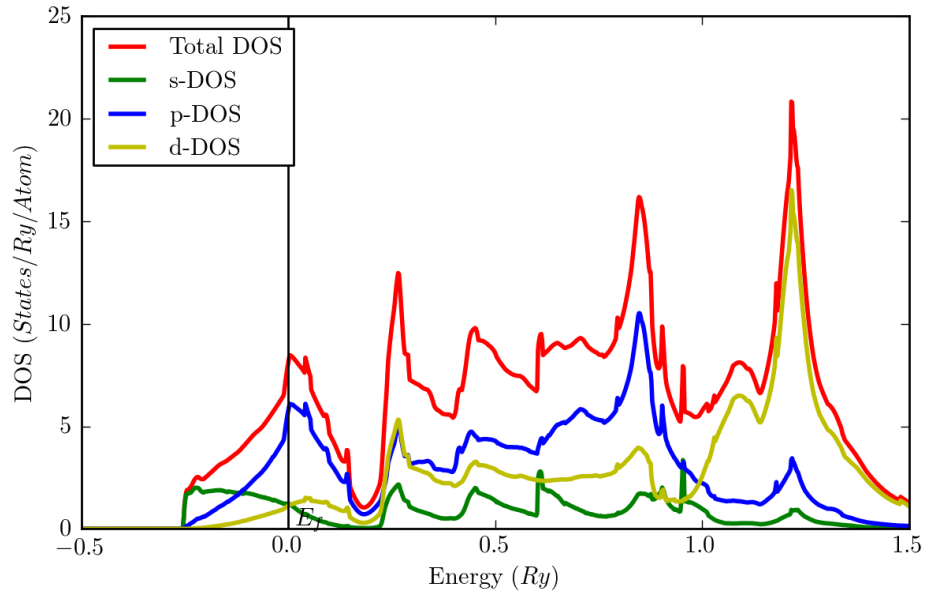


Figure 6.8: Density of States of Lithium calculated using NRL-TB at equilibrium lattice constant $a = 6.60$ a.u. All eigenvalues are shifted so that the Fermi level is at zero.

Using the value of DOS, the electronic specific heat coefficient of Li is calculated to be $1.52 \text{ mJ}/(\text{mol deg}^2)$ using the Eq. (2.41), which is in good agreement with experimental value of γ from Kittel [25] is $1.63 \text{ mJ}/(\text{mol deg}^2)$.

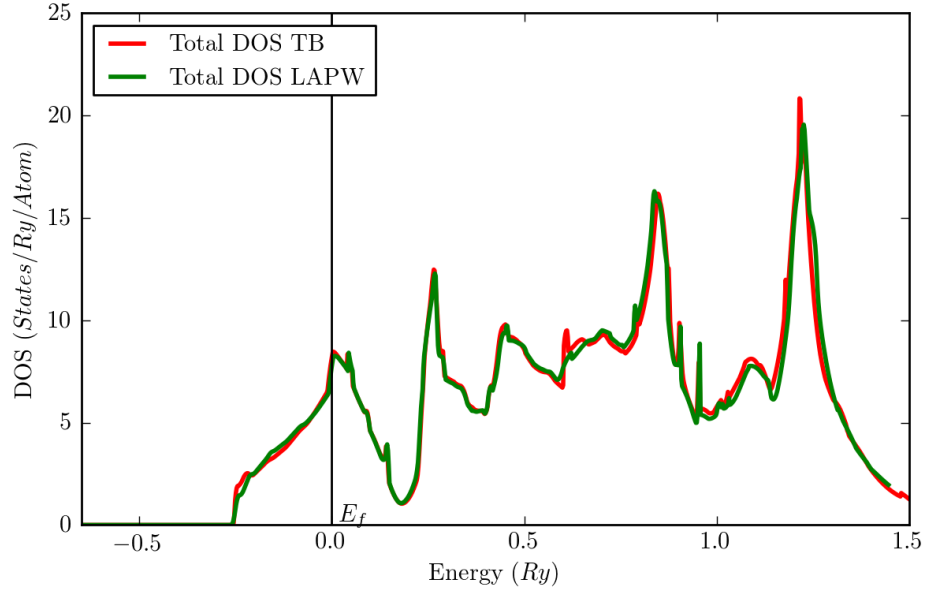


Figure 6.9: Density of States of Lithium calculated using LAPW-GGA and NRL-TB parameters at equilibrium lattice constant $a = 6.60$ a.u.

6.8 Vacancy Formation Energy

The VFE for Sr has been tested via a relaxed super-cell method with conjugate gradient approximation, in which the energy of a cell with a complete lattice is compared to a lattice in which one atom has been removed. The VFE indicates the stability of the structure due to the loss of an atom; a positive value means that the structure is more stable in the full lattice configuration.

Using the NRL-TB parameters, the VFE has been calculated to be -0.04 eV. This negative value may be indicative that this study has not considered the 9R structure.

6.9 Enthalpy

Enthalpy has been calculated for both fcc and bcc structures of Li, and the difference between enthalpies has been plotted v. pressure in Fig. 6.10. An intersection between the enthalpies is observed, and it is found at pressure of 4.19 GPa. This intersection

indicates a phase change, and is 45% smaller than that measured by Stager et al. [107] at 7.00 GPa. This has been confirmed by X-ray diffraction measurements performed by Olinger et al. [108], which show a transformation to the fcc structure near 7.00 GPa. However, when compared with transition metals, which have transitions pressures in triple digits, this variation is comparable.

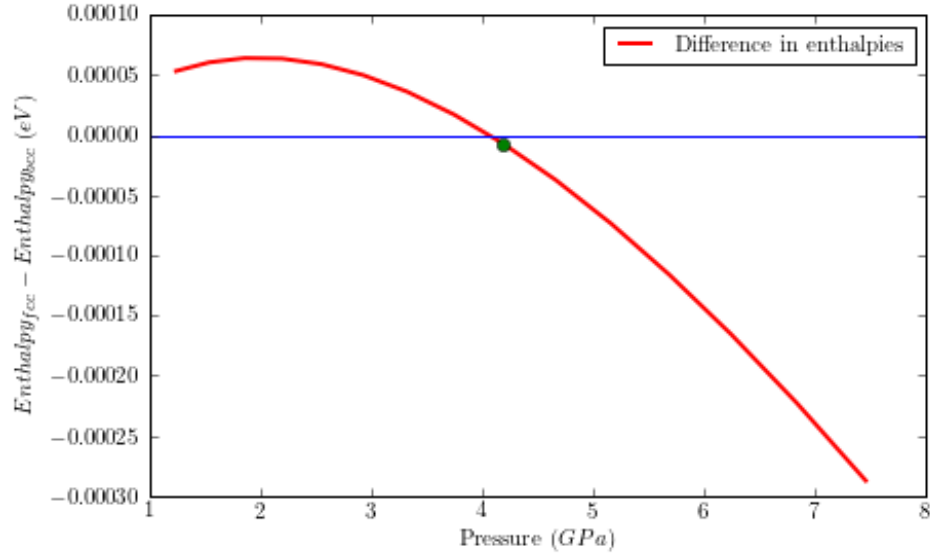


Figure 6.10: Difference in enthalpy for Lithium plotted against pressure in GPa.

6.10 Phonon Frequencies

Unlike Sr, Ca, and Rb, the phonon frequencies obtained for Li have imaginary values. Like with elastic constants, this indicates the instability of the bcc structure under ambient conditions.

6.11 Summary

Overall, the application of NRL-TB parameterization method on Li has been successful in predicting equilibrium lattice constant, bulk modulus, energy bands, DOS and en-

thalpy. The negative elastic constants suggest that the bcc structure for Li is unstable. Also, unphysical results were obtained for the VFE and phonon frequencies. There is a lack of good understanding of this failure. It could be due to the softness of the material or the fact that the d-orbitals are omitted in the Hamiltonian, a choice, which is reasonable since the d-states are far above the Fermi level. This TB parametrization may favor the complicated 9R structure, which will be the subject of future investigation.

Chapter 7: Conclusions

In this dissertation, the Naval Research Laboratory (NRL)-Tight-Binding (TB) method has been successfully applied to alkaline earth metals Strontium (Sr) and Calcium (Ca), and alkali metals Rubidium (Rb) and Lithium (Li). A detailed analysis of each element has been presented, including band structure, Density of States (DOS), elastic constants, bulk modulus, phonon frequencies, enthalpy, Molecular Dynamics (MD), Mean Square Displacement (MSD), and Vacancy Formation Energy (VFE). In this Chapter, a summary of the results of each element is outlined and direction for future work is provided.

7.1 Alkaline Earth Metal: Strontium

Using Linear Augmented Plane Wave (LAPW)-Generalized Gradient Approximation (GGA) first principles values as input, transferable NRL-TB parameters are generated, which have improved on those previously generated using LAPW-Local Density Approximation (LDA). These new NRL-TB parameters confirm the ground state of Sr as face centered cubic (fcc), having lattice constant, which is only 0.082% smaller than experiment. The transferable TB parameters have predicted total energies of various structures that are not originally included in the fit. Sr being a very soft element, the elastic constants were difficult to predict using LDA, but NRL-TB calculations using GGA have shown $C_{11} - C_{12}$ to be within 8% of experiment. The value of C_{44} is almost 50% higher, but it is within the absolute error margin of this parametrization method of ± 10 GPa. Energy bands predicted using the TB parameters are in good agreement with first principles inputs, and so are DOS values. Also, the semi-metal property of Sr has been predicted. Tight-Binding Molecular Dynamics (TBMD), which has been a challenge with the earlier set of TB parameters, is now possible and also predicts with

reasonable accuracy, the transition temperature of Sr from fcc to bcc around 800K. Also, the MSD calculations are in good agreement with experiment. Enthalpy calculations have shown that Sr transitions from fcc to bcc under pressure. However, since Sr is an extremely soft material, even though the transition pressure predicted is much smaller than that measured by experiment, it is still within the error margin. The computational time to calculate VFE is much smaller than other methods, and it is in excellent agreement with VFE calculated using the Embedded Atom Method (EAM). Phonon frequencies are within $\pm 10\%$ agreement with experiment. Also, behavior of phonon frequencies under pressure have been predicted.

7.2 Alkaline Earth Metal: Calcium

Unlike Sr, Ca required more first principles inputs to predict accurately the ground state as fcc. The lattice constant calculated is in excellent agreement with experiment, and the TB parameters predict total energies of structures, which are not included in the fit. Elastic constants are in reasonable agreement with experiment. A second set of TB parameters were generated, for better results with respect to bands energies and DOS. This second set of TB parameters predicts band energies, which are in good agreement with first principles calculations. Also, DOS values calculated using these transferable TB parameters are a good match to LAPW-GGA inputs. Like Sr, TBMD of Ca was expected to stop at transition temperature of 700K, however, use of the repulsive potential allows TBMD to predict melting temperature of 1200K. Calculations of enthalpies show transition of Ca from fcc to bcc under pressure, and as with Sr, even though it is much smaller than experiment, it is within the error margin of the parametrization method used. VFE is also in good agreement with other calculations and so are phonon frequencies. Also predicted are phonon frequencies, which show an upward trend with increase in pressure.

7.3 Alkali Metal: Rubidium

The NRL-TB method had never previously applied to alkali metals like Rb. The first principles calculation results influence prediction of the ground state as hcp, instead of bcc. The difference in energy between hcp, fcc and bcc structures are so minute that it can be considered within the noise of the calculation. The lattice constant of 5.688 Bohr is in excellent agreement with experiment, and so is the bulk modulus. Like with Ca, a second set of transferable TB parameters is used in calculations of the band energies and DOS, which have provided better agreement with values generated using LAPW-GGA. Being very soft, the elastic constants of Rb are extremely small compared to those of transition metals (100 – 1000 times smaller), and hence, current predictions of $C_{11} - C_{12}$ are in reasonable agreement with experiment. Using a repulsive potential within the TBMD, a melting point temperature in close match to the measured value is predicted, and also MSD is in good agreement with experiment. Similar to Sr and Ca, enthalpy calculation of Rb has shown a phase transition with change in pressure, but from bcc to fcc. However, unlike alkaline earth metals, phonon frequencies have shown a downward trend under pressure.

7.4 Alkali Metal: Lithium

Like Rb, the NRL-TB method had never previously applied to the smallest metal Li. The difference in energy among hcp, fcc, and bcc structures are so minute that it can be considered within the noise of the calculation. Overall, the application of NRL-TB parameterization method on Li has been successful in predicting equilibrium lattice constant, bulk modulus, energy bands, DOS, and enthalpy. The negative elastic constants suggest that the bcc structure is unstable, and this TB parametrization may favor the complicated 9R structure, which will be the subject of future investigation.

7.5 Future Work

Natural extension of this work is the application of the NRL-TB parametrization method to study other alkali metals like Potassium (K) and Sodium (Na), which like Li, also transform into a 9R structure [110]. Also, more detailed calculations can be performed on alkaline earth metals like Magnesium (Mg) and Barium (Ba) using LAPW-GGA as inputs. For the elements in this dissertation, an additional study would be to calculate in detail the dispersion curves of phonon frequencies, rather than only at the high frequency q-points. Also, a comprehensive study the effect of higher pressure on phase transitions of these elements is necessary. Li and other alkali metals like K and Na require further comprehensive investigation especially for the 9R structure.

Chapter A: Appendix

A.1 Parameters for Strontium

```
NN00000                                (Old style Overlap Parameters)

Strontium (Sr)

1
16.5   0.5                                (RCUT and SCREENL for 1-1 interactions)
9                                             (Orbitals for atom 1)
87.62                                       (Atomic Weight of Atom 1)
2.0   0.0   0.0                           (formal spd valence occupancy for atom1)

  0.108583087236E+01   0  1      lamda
  0.872346840141E-01   0  2      a_s
-0.102856166957E+02   0  3      b_s
  0.195504786487E+04   0  4      c_s
-0.740796188805E+05   0  5      d_s
  0.147686896112E+00   0  6      a_p
  0.314197498278E+02   0  7      b_p
-0.134606020721E+04   0  8      c_p
  0.155103307634E+05   0  9      d_p
  0.253802326700E+00   0 10      a_t2g
-0.539065970177E+00   0 11      b_t2g
-0.520050833658E+03   0 12      c_t2g
  0.443865120511E+05   0 13      d_t2g
  0.253802326700E+00   0 14      a_eg
-0.539065970177E+00   1 15      b_eg
-0.520050833658E+03   2 16      c_eg
  0.443865120511E+05   3 17      d_eg
  0.115149637313E+03   0 18      e_{ss sigma}
```

-0.130411648720E+02	0 19	f_{ss sigma}
-0.825584696612E+00	0 20	fbar_{ss sigma}
0.937480465747E+00	0 21	g_{ss sigma}
-0.711604509267E+01	0 22	e_{sp sigma}
0.127555806931E+01	0 23	f_{sp sigma}
-0.116575123453E-01	0 24	fbar_{sp sigma}
0.745873461605E+00	0 25	g_{sp sigma}
0.133406984598E-01	0 26	e_{pp sigma}
0.208971693727E-02	0 27	f_{pp sigma}
-0.246775721150E-03	0 28	fbar_{pp sigma}
0.102575001527E+00	1 29	g_{pp sigma}
-0.660684425677E+02	0 30	e_{pp pi}
0.572429597286E+01	0 31	f_{pp pi}
-0.113393347961E+01	0 32	fbar_{pp pi}
0.101238263150E+01	1 33	g_{pp pi}
0.205075242882E+01	0 34	e_{sd sigma}
-0.353155429233E+00	0 35	f_{sd sigma}
-0.160447655597E-02	0 36	fbar_{sd sigma}
0.676277467450E+00	0 37	g_{sd sigma}
0.253097166940E+01	0 38	e_{pd sigma}
-0.344457165927E+00	0 39	f_{pd sigma}
-0.215840190552E-02	0 40	fbar_{pd sigma}
0.722353658959E+00	0 41	g_{pd sigma}
0.362070050561E+00	0 42	e_{pd pi}
-0.163575113654E-01	0 43	f_{pd pi}
-0.799590331646E-03	0 44	fbar_{pd pi}
0.540235530126E+00	0 45	g_{pd pi}
-0.136944047077E+02	0 46	e_{dd sigma}
0.184511818820E+01	0 47	f_{dd sigma}
-0.816857544059E-01	0 48	fbar_{dd sigma}

0.839388588618E+00	0 49	$g_{\{dd\} \sigma}$
-0.409601389337E+01	0 50	$e_{\{dd\} \pi}$
0.119045858424E+01	0 51	$f_{\{dd\} \pi}$
-0.129518350729E-01	0 52	$\bar{f}_{\{dd\} \pi}$
0.824823700615E+00	0 53	$g_{\{dd\} \pi}$
0.175046643467E+03	0 54	$e_{\{dd\} \Delta}$
0.944707785253E+01	0 55	$f_{\{dd\} \Delta}$
-0.459185558355E+01	0 56	$\bar{f}_{\{dd\} \Delta}$
0.103210682695E+01	0 57	$g_{\{dd\} \Delta}$
0.918304462724E+01	0 58	$e_{\{ss\} \sigma}$
-0.143882361353E+01	0 59	$f_{\{ss\} \sigma}$
0.578928742247E-01	0 60	$\bar{f}_{\{ss\} \sigma}$
0.583232781765E+00	0 61	$g_{\{ss\} \sigma}$
0.255208126324E+04	0 62	$e_{\{sp\} \sigma}$
-0.146049987474E+03	0 63	$f_{\{sp\} \sigma}$
-0.420751799740E+02	0 64	$\bar{f}_{\{sp\} \sigma}$
0.105684096460E+01	1 65	$g_{\{sp\} \sigma}$
0.745381048486E+03	0 66	$e_{\{pp\} \sigma}$
-0.111378233396E+03	0 67	$f_{\{pp\} \sigma}$
0.292527181606E+00	0 68	$\bar{f}_{\{pp\} \sigma}$
0.917507094298E+00	0 69	$g_{\{pp\} \sigma}$
0.424346102168E+05	0 70	$e_{\{pp\} \pi}$
0.303431500672E+05	0 71	$f_{\{pp\} \pi}$
-0.956493916751E+04	0 72	$\bar{f}_{\{pp\} \pi}$
0.149475899805E+01	0 73	$g_{\{pp\} \pi}$
0.104959853980E+01	0 74	$e_{\{sd\} \sigma}$
-0.168493415909E+00	0 75	$f_{\{sd\} \sigma}$
0.666815455043E-02	0 76	$\bar{f}_{\{sd\} \sigma}$
0.101368687502E+00	1 77	$g_{\{sd\} \sigma}$
-0.144170836009E+03	0 78	$e_{\{pd\} \sigma}$

0.273717139837E+01	0 79	f_{pd sigma}
0.312513277590E+01	0 80	fbar_{pd sigma}
0.894019876167E+00	0 81	g_{pd sigma}
-0.156325665883E+02	0 82	e_{pd pi}
0.202457400190E+01	0 83	f_{pd pi}
-0.217460525778E+00	0 84	fbar_{pd pi}
0.850568238460E+00	0 85	g_{pd pi}
-0.683140486286E+02	0 86	e_{dd sigma}
0.279424035280E+01	0 87	f_{dd sigma}
0.109039573958E+01	0 88	fbar_{dd sigma}
0.828645151036E+00	0 89	g_{pp sigma}
0.387645529761E+03	0 90	e_{dd pi}
-0.261098008816E+02	0 91	f_{dd pi}
-0.634313236762E+01	0 92	fbar_{dd pi}
0.100023759742E+01	0 93	g_{pd pi}
0.969424655613E+03	0 94	e_{dd delta}
-0.330032360717E+02	0 95	f_{dd delta}
-0.107735030205E+02	0 96	fbar_{dd delta}
0.106179354689E+01	1 97	g_{dd delta} \\

A.2 Parameters for Calcium: Total Energies Only

NN00000	(Old style Overlap Parameters)
Calcium (Ca)	
1	(One atom type in this file)
16.5 0.5	(RCUT and SCREENL for 1-1 interactions)
9	(Orbitals for atom 1)
40.08	(Atomic Weight of Atom 1)
2.0 0.0 0.0	(formal spd valence occupancy for atom 1)
0.108770914822E+01 0 1	lamda
0.191198542401E+00 0 2	a_s

-0.722506513586E+01	0	3	b_s
0.910944512562E+03	0	4	c_s
-0.136304180800E+05	0	5	d_s
0.783922941802E-01	0	6	a_p
0.254857097326E+02	0	7	b_p
-0.602113972020E+03	0	8	c_p
0.192650441117E+05	0	9	d_p
0.143847483298E+00	0	10	a_t2g
0.146042089247E+02	0	11	b_t2g
-0.540307757950E+03	0	12	c_t2g
0.716957917792E+04	0	13	d_t2g
0.143847483298E+00	0	14	a_eg
0.146042089247E+02	1	15	b_eg
-0.540307757950E+03	2	16	c_eg
0.716957917792E+04	3	17	d_eg
0.102988708682E+02	0	18	e_{ss sigma}
0.149684588334E+01	0	19	f_{ss sigma}
-0.715909057383E+00	0	20	fbar_{ss sigma}
0.860201941886E+00	0	21	g_{ss sigma}
-0.466533903907E+01	0	22	e_{sp sigma}
-0.171999743090E+00	0	23	f_{sp sigma}
0.285570901624E+00	0	24	fbar_{sp sigma}
0.837034909999E+00	0	25	g_{sp sigma}
0.313035573154E+02	0	26	e_{pp sigma}
-0.164741049360E+01	0	27	f_{pp sigma}
0.157461744098E+01	0	28	fbar_{pp sigma}
0.102575001527E+01	1	29	g_{pp sigma}
-0.538715656760E+03	0	30	e_{pp pi}
0.153081057699E+03	0	31	f_{pp pi}
-0.117643441521E+02	0	32	fbar_{pp pi}
0.101238263150E+01	1	33	g_{pp pi}

-0.114321568248E+01	0 34	e_{sd sigma}
-0.405150632107E+00	0 35	f_{sd sigma}
0.211128359905E-01	0 36	fbar_{sd sigma}
0.795270613179E+00	0 37	g_{sd sigma}
-0.439485371550E+03	0 38	e_{pd sigma}
0.177365131068E+03	0 39	f_{pd sigma}
-0.173087959056E+02	0 40	fbar_{pd sigma}
0.101880113504E+01	1 41	g_{pd sigma}
0.166352493505E+02	0 42	e_{pd pi}
-0.123004895027E+01	0 43	f_{pd pi}
0.187027649290E+00	0 44	fbar_{pd pi}
0.965635178940E+00	0 45	g_{pd pi}
-0.228991757800E+04	0 46	e_{dd sigma}
0.706457778244E+03	0 47	f_{dd sigma}
-0.564903814644E+02	0 48	fbar_{dd sigma}
0.107276012393E+01	1 49	g_{dd sigma}
-0.358208142671E+02	0 50	e_{dd pi}
0.311806157665E+01	0 51	f_{dd pi}
0.495029468948E+00	0 52	fbar_{dd pi}
0.978195693666E+00	0 53	g_{dd pi}
0.433681810600E+03	0 54	e_{dd delta}
-0.105379445577E+03	0 55	f_{dd delta}
0.562513193968E+01	0 56	fbar_{dd delta}
0.102752696642E+01	1 57	g_{dd delta}
-0.294576250368E+03	0 58	e_{ss sigma}
0.221938266211E+02	0 59	f_{ss sigma}
0.491599998487E+01	0 60	fbar_{ss sigma}
0.928295454978E+00	0 61	g_{ss sigma}
0.169227773109E+04	0 62	e_{sp sigma}
-0.141196113272E+03	0 63	f_{sp sigma}

-0.253477361034E+02	0 64	fbar_{sp sigma}
0.105684096460E+01	1 65	g_{sp sigma}
0.162085418734E+04	0 66	e_{pp sigma}
-0.179135282331E+03	0 67	f_{pp sigma}
-0.154167825465E+02	0 68	fbar_{pp sigma}
0.102321889386E+01	0 69	g_{pp sigma}
-0.607706564882E+04	0 70	e_{pp pi}
0.163138489615E+04	0 71	f_{pp pi}
-0.101642626319E+03	0 72	fbar_{pp pi}
0.106970497340E+01	1 73	g_{pp pi}
0.224169764708E+03	0 74	e_{sd sigma}
-0.106835877232E+03	0 75	f_{sd sigma}
0.124679294610E+02	0 76	fbar_{sd sigma}
0.101368687502E+01	1 77	g_{sd sigma}
0.516509915138E+02	0 78	e_{pd sigma}
-0.635513410257E+02	0 79	f_{pd sigma}
0.763534809051E+01	0 80	fbar_{pd sigma}
0.104271487073E+01	0 81	g_{pd sigma}
0.914248943971E+03	0 82	e_{pd pi}
-0.931236629202E+02	0 83	f_{pd pi}
-0.899786036147E+01	0 84	fbar_{pd pi}
0.104142445979E+01	1 85	g_{pd pi}
0.623605162945E+05	0 86	e_{dd sigma}
-0.606324716024E+05	0 87	f_{dd sigma}
0.909187877872E+04	0 88	fbar_{dd sigma}
0.148611679756E+01	0 89	g_{pp sigma}
0.640489355795E+03	0 90	e_{dd pi}
-0.165446526108E+03	0 91	f_{dd pi}
0.412923467759E+01	0 92	fbar_{dd pi}
0.107950634834E+01	1 93	g_{pd pi}

0.271127915208E+04	0 94	e_{dd delta}
-0.709029642783E+03	0 95	f_{dd delta}
0.445654844102E+02	0 96	fbar_{dd delt
0.106179354689E+01	1 97	g_{dd delta}

A.3 Parameters for Calcium: Bands Only

NN00000	(Old style Overlap Parameters)
Calcium (Ca)	
1	(One atom type in this file)
16.5 0.5	(RCUT and SCREENL for 1-1 interactions)
9	(Orbitals for atom 1)
40.08	(Atomic Weight of Atom 1)
2.0 0.0 0.0	(formal spd valence occupancy for atom 1)
0.108786399491E+01	0 1 lamda
0.188123736444E+00	0 2 a_s
-0.741681509871E+01	0 3 b_s
0.898986485040E+03	0 4 c_s
-0.143886051275E+05	0 5 d_s
0.778414890106E-01	0 6 a_p
0.254513789898E+02	0 7 b_p
-0.604254551554E+03	0 8 c_p
0.191321884473E+05	0 9 d_p
0.144265230977E+00	0 10 a_t2g
0.146302506071E+02	0 11 b_t2g
-0.538684882212E+03	0 12 c_t2g
0.726968416692E+04	0 13 d_t2g
0.144265230977E+00	0 14 a_eg
0.146302506071E+02	1 15 b_eg
-0.538684882212E+03	2 16 c_eg
0.726968416692E+04	3 17 d_eg
0.105304819290E+02	0 18 e_{ss sigma}

0.153206417490E+01	0 19	f_{ss sigma}
-0.710274244292E+00	0 20	fbar_{ss sigma}
0.862693039633E+00	0 21	g_{ss sigma}
-0.457682450026E+01	0 22	e_{sp sigma}
-0.160058979121E+00	0 23	f_{sp sigma}
0.287175419688E+00	0 24	fbar_{sp sigma}
0.836323662210E+00	0 25	g_{sp sigma}
0.312160780555E+02	0 26	e_{pp sigma}
-0.165694847401E+01	0 27	f_{pp sigma}
0.157379960470E+01	0 28	fbar_{pp sigma}
0.102575001527E+01	1 29	g_{pp sigma}
-0.540928684783E+03	0 30	e_{pp pi}
0.152785413334E+03	0 31	f_{pp pi}
-0.118036024549E+02	0 32	fbar_{pp pi}
0.101238263150E+01	1 33	g_{pp pi}
-0.121482210864E+01	0 34	e_{sd sigma}
-0.414547705022E+00	0 35	f_{sd sigma}
0.198914822959E-01	0 36	fbar_{sd sigma}
0.793323272214E+00	0 37	g_{sd sigma}
-0.437842951895E+03	0 38	e_{pd sigma}
0.177575466812E+03	0 39	f_{pd sigma}
-0.172828305270E+02	0 40	fbar_{pd sigma}
0.101880113504E+01	1 41	g_{pd sigma}
0.165872445965E+02	0 42	e_{pd pi}
-0.123604202844E+01	0 43	f_{pd pi}
0.186301173315E+00	0 44	fbar_{pd pi}
0.965797993137E+00	0 45	g_{pd pi}
-0.226534912510E+04	0 46	e_{dd sigma}
0.709491939728E+03	0 47	f_{dd sigma}
-0.561381978772E+02	0 48	fbar_{dd sigma}

0.107276012393E+01	1 49	$g_{\{dd\} \sigma}$
-0.348030179404E+02	0 50	$e_{\{dd\} \pi}$
0.325942914921E+01	0 51	$f_{\{dd\} \pi}$
0.514735359157E+00	0 52	$\bar{f}_{\{dd\} \pi}$
0.972529336870E+00	0 53	$g_{\{dd\} \pi}$
0.438236914335E+03	0 54	$e_{\{dd\} \Delta}$
-0.104764210687E+03	0 55	$f_{\{dd\} \Delta}$
0.570809996926E+01	0 56	$\bar{f}_{\{dd\} \Delta}$
0.102752696642E+01	1 57	$g_{\{dd\} \Delta}$
-0.294361355941E+03	0 58	$e_{\{ss\} \sigma}$
0.222279490099E+02	0 59	$f_{\{ss\} \sigma}$
0.492176009814E+01	0 60	$\bar{f}_{\{ss\} \sigma}$
0.927958456934E+00	0 61	$g_{\{ss\} \sigma}$
0.164305901812E+04	0 62	$e_{\{sp\} \sigma}$
-0.147694219519E+03	0 63	$f_{\{sp\} \sigma}$
-0.261941418875E+02	0 64	$\bar{f}_{\{sp\} \sigma}$
0.105684096460E+01	1 65	$g_{\{sp\} \sigma}$
0.171554163474E+04	0 66	$e_{\{pp\} \sigma}$
-0.166202690013E+03	0 67	$f_{\{pp\} \sigma}$
-0.136428741240E+02	0 68	$\bar{f}_{\{pp\} \sigma}$
0.103821801580E+01	0 69	$g_{\{pp\} \sigma}$
-0.616595467208E+04	0 70	$e_{\{pp\} \pi}$
0.161340996962E+04	0 71	$f_{\{pp\} \pi}$
-0.105188512832E+03	0 72	$\bar{f}_{\{pp\} \pi}$
0.106970497340E+01	1 73	$g_{\{pp\} \pi}$
0.247844468490E+03	0 74	$e_{\{sd\} \sigma}$
-0.104788670041E+03	0 75	$f_{\{sd\} \sigma}$
0.125246999454E+02	0 76	$\bar{f}_{\{sd\} \sigma}$
0.101368687502E+01	1 77	$g_{\{sd\} \sigma}$
0.102624736072E+03	0 78	$e_{\{pd\} \sigma}$

-0.568550212715E+02	0 79	f_{pd sigma}
0.850115734348E+01	0 80	fbar_{pd sigma}
0.110831636770E+01	0 81	g_{pd sigma}
0.970439761913E+03	0 82	e_{pd pi}
-0.855033159430E+02	0 83	f_{pd pi}
-0.796045912100E+01	0 84	fbar_{pd pi}
0.104142445979E+01	1 85	g_{pd pi}
0.247975414187E+06	0 86	e_{dd sigma}
-0.517919344152E+05	0 87	f_{dd sigma}
0.958008315312E+04	0 88	fbar_{dd sigma}
0.146497394433E+01	0 89	g_{pp sigma}
0.688394506077E+03	0 90	e_{dd pi}
-0.159346602291E+03	0 91	f_{dd pi}
0.488276563573E+01	0 92	fbar_{dd pi}
0.107950634834E+01	1 93	g_{pd pi}
0.272225021663E+04	0 94	e_{dd delta}
-0.707416809376E+03	0 95	f_{dd delta}
0.448027752843E+02	0 96	fbar_{dd delta}
0.106179354689E+01	1 97	g_{dd delta}

A.4 Parameters for Rubidium: Total Energies Only

```

NN00000                                (Old style Overlap Parameters)

Rubidium (Rb)

1
16.5   0.5                                (RCUT and SCREENL for 1-1 interactions)
9                                             (Orbitals for atom 1)
85.4678                                (Atomic Weight of Atom 1)
1.0   0.0   0.0                        (formal spd valence occupancy for atom1)
0.109656120874E+01    0  1              lamda
0.470840021769E-01    0  2              a_s

```


0.102221570900E+02	0 3	b_s
-0.431191654374E+03	0 4	c_s
0.676324029359E+05	0 5	d_s
0.252296957080E+00	0 6	a_p
0.195910218966E+02	0 7	b_p
-0.763533130347E+03	0 8	c_p
0.886575722000E+04	0 9	d_p
0.462171375445E+00	0 10	a_t2g
-0.675123757126E+02	0 11	b_t2g
-0.243969783442E+05	0 12	c_t2g
0.115614061486E+08	0 13	d_t2g
0.462171375445E+00	0 14	a_eg
-0.675123757126E+02	1 15	b_eg
-0.243969783442E+05	2 16	c_eg
0.115614061486E+08	3 17	d_eg
-0.191475043179E+01	0 18	e_{ss sigma}
-0.357879009821E+00	0 19	f_{ss sigma}
-0.616110697254E-01	0 20	fbar_{ss sigma}
0.837255025418E+00	1 21	g_{ss sigma}
-0.104556504243E+02	0 22	e_{sp sigma}
-0.687505491923E+00	0 23	f_{sp sigma}
0.259710951273E+00	0 24	fbar_{sp sigma}
0.771995074491E+00	1 25	g_{sp sigma}
0.203973651072E+04	0 26	e_{pp sigma}
-0.273906316701E+03	0 27	f_{pp sigma}
0.758193779640E+01	0 28	fbar_{pp sigma}
0.102575001527E+01	1 29	g_{pp sigma}
-0.136908600561E+04	0 30	e_{pp pi}
0.424285378065E+03	0 31	f_{pp pi}
-0.324841444870E+02	0 32	fbar_{pp pi}
0.101238263150E+01	1 33	g_{pp pi}

-0.849180606986E+03	0 34	e_{sd sigma}
0.206399365295E+02	0 35	f_{sd sigma}
0.861331230232E+01	0 36	fbar_{sd sigma}
0.104252201664E+01	1 37	g_{sd sigma}
0.839679532478E+03	0 38	e_{pd sigma}
0.267477351618E+03	0 39	f_{pd sigma}
-0.388358130657E+02	0 40	fbar_{pd sigma}
0.101880113504E+01	1 41	g_{pd sigma}
0.146559284209E+00	0 42	e_{pd pi}
-0.173350523268E+01	0 43	f_{pd pi}
0.201377186935E+00	0 44	fbar_{pd pi}
0.753018746804E+00	1 45	g_{pd pi}
-0.155207786613E+05	0 46	e_{dd sigma}
0.304846386632E+04	0 47	f_{dd sigma}
-0.137440273980E+03	0 48	fbar_{dd sigma}
0.107276012393E+01	1 49	g_{dd sigma}
-0.328829417161E+03	0 50	e_{dd pi}
-0.109538536434E+01	0 51	f_{dd pi}
0.550568105645E+01	0 52	fbar_{dd pi}
0.946670212704E+00	1 53	g_{dd pi}
0.304333736623E+03	0 54	e_{dd delta}
-0.428912718897E+03	0 55	f_{dd delta}
0.401214605624E+02	0 56	fbar_{dd delta}
0.102752696642E+01	1 57	g_{dd delta}
-0.145627662031E+04	0 58	e_{ss sigma}
0.390994246340E+02	0 59	f_{ss sigma}
0.166207783961E+02	0 60	fbar_{ss sigma}
0.934025772177E+00	1 61	g_{ss sigma}
0.148622131441E+05	0 62	e_{sp sigma}
-0.402905967775E+03	0 63	f_{sp sigma}

-0.184357568129E+03	0 64	fbar_{sp sigma}
0.105684096460E+01	1 65	g_{sp sigma}
0.154749242124E+04	0 66	e_{pp sigma}
-0.126788972306E+03	0 67	f_{pp sigma}
-0.726228838970E+01	0 68	fbar_{pp sigma}
0.878497145096E+00	1 69	g_{pp sigma}
-0.464902816795E+04	0 70	e_{pp pi}
0.996194907294E+03	0 71	f_{pp pi}
-0.505747820959E+02	0 72	fbar_{pp pi}
0.106970497340E+01	1 73	g_{pp pi}
-0.797426202166E+04	0 74	e_{sd sigma}
-0.950539510081E+02	0 75	f_{sd sigma}
0.128908745183E+03	0 76	fbar_{sd sigma}
0.101368687502E+01	1 77	g_{sd sigma}
-0.643762159174E+03	0 78	e_{pd sigma}
-0.624364870574E+02	0 79	f_{pd sigma}
0.157608392023E+02	0 80	fbar_{pd sigma}
0.943864321191E+00	1 81	g_{pd sigma}
0.414648312924E+04	0 82	e_{pd pi}
-0.540160626167E+03	0 83	f_{pd pi}
0.261554208654E+01	0 84	fbar_{pd pi}
0.104142445979E+01	1 85	g_{pd pi}
0.191649908586E+04	0 86	e_{dd sigma}
-0.218790162807E+04	0 87	f_{dd sigma}
0.241326766704E+03	0 88	fbar_{dd sigma}
0.100373167180E+01	1 89	g_{pp sigma}
-0.345209739452E+03	0 90	e_{dd pi}
0.107701149712E+02	0 91	f_{dd pi}
-0.321744517575E+01	0 92	fbar_{dd pi}
0.107950634834E+01	1 93	g_{pd pi}

-0.205837751826E+04	0 94	e_{dd delta}
0.166996245964E+03	0 95	f_{dd delta}
0.195226869344E+02	0 96	fbar_{dd delt
0.106179354689E+01	1 97	g_{dd delta}

A.5 Parameters for Rubidium: Bands Only

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NN00000                                (Old style Overlap Parameters)

Rubidium (Rb)

1
16.5   0.5                                (RCUT and SCREENL for 1-1 interactions)
9                                             (Orbitals for atom 1)
85.4678                                (Atomic Weight of Atom 1)
1.0   0.0   0.0                            (formal spd valence occupancy for atom1)

0.109631746351E+01    0  1    lamda
0.466354030234E-01    0  2    a_s
0.102312332984E+02    0  3    b_s
-0.606505488552E+03    0  4    c_s
0.102864154743E+07    0  5    d_s
0.248057514056E+00    0  6    a_p
0.153245287494E+02    0  7    b_p
-0.283262177368E+04    0  8    c_p
-0.192080070890E+07    0  9    d_p
0.454146562842E+00    0 10    a_t2g
-0.622376848718E+02    0 11    b_t2g
-0.259498653114E+05    0 12    c_t2g
0.986282494501E+07    0 13    d_t2g
0.454146562842E+00    0 14    a_eg
-0.622376848718E+02    1 15    b_eg
-0.259498653114E+05    2 16    c_eg
0.986282494501E+07    3 17    d_eg
-0.180939725871E+01    0 18    e_{ss sigma}

```

-0.599575324469E+00	0 19	f_{ss sigma}
-0.116854374273E+00	0 20	fbar_{ss sigma}
0.837255025418E+00	1 21	g_{ss sigma}
-0.103896189875E+02	0 22	e_{sp sigma}
-0.745524866142E+00	0 23	f_{sp sigma}
0.246540765823E+00	0 24	fbar_{sp sigma}
0.771995074491E+00	1 25	g_{sp sigma}
0.111327730317E+04	0 26	e_{pp sigma}
-0.289701405198E+03	0 27	f_{pp sigma}
0.154800656605E+02	0 28	fbar_{pp sigma}
0.102575001527E+01	1 29	g_{pp sigma}
-0.130008065282E+04	0 30	e_{pp pi}
0.427892607985E+03	0 31	f_{pp pi}
-0.324385104310E+02	0 32	fbar_{pp pi}
0.101238263150E+01	1 33	g_{pp pi}
-0.335276381808E+03	0 34	e_{sd sigma}
0.160879116901E+02	0 35	f_{sd sigma}
0.129516710888E+01	0 36	fbar_{sd sigma}
0.104252201664E+01	1 37	g_{sd sigma}
0.346001135334E+03	0 38	e_{pd sigma}
0.287360074686E+03	0 39	f_{pd sigma}
-0.282909964789E+02	0 40	fbar_{pd sigma}
0.101880113504E+01	1 41	g_{pd sigma}
0.705238239295E+01	0 42	e_{pd pi}
-0.170510704029E+01	0 43	f_{pd pi}
0.130914765103E+00	0 44	fbar_{pd pi}
0.753018746804E+00	1 45	g_{pd pi}
-0.124955978213E+05	0 46	e_{dd sigma}
0.306080903509E+04	0 47	f_{dd sigma}
-0.171593340633E+03	0 48	fbar_{dd sigma}

0.107276012393E+01	1 49	$g_{\{dd\} \sigma}$
-0.518676414841E+03	0 50	$e_{\{dd\} \pi}$
-0.562363466144E+01	0 51	$f_{\{dd\} \pi}$
0.684081309600E+01	0 52	$\bar{f}_{\{dd\} \pi}$
0.946670212704E+00	1 53	$g_{\{dd\} \pi}$
0.136923107191E+04	0 54	$e_{\{dd\} \Delta}$
-0.427958051897E+03	0 55	$f_{\{dd\} \Delta}$
0.274014851484E+02	0 56	$\bar{f}_{\{dd\} \Delta}$
0.102752696642E+01	1 57	$g_{\{dd\} \Delta}$
-0.108112389046E+04	0 58	$e_{\{ss\} \sigma}$
0.409442069613E+02	0 59	$f_{\{ss\} \sigma}$
0.121042076836E+02	0 60	$\bar{f}_{\{ss\} \sigma}$
0.934025772177E+00	1 61	$g_{\{ss\} \sigma}$
0.243636390678E+05	0 62	$e_{\{sp\} \sigma}$
-0.426260124011E+03	0 63	$f_{\{sp\} \sigma}$
-0.304548539356E+03	0 64	$\bar{f}_{\{sp\} \sigma}$
0.105684096460E+01	1 65	$g_{\{sp\} \sigma}$
0.187916966500E+04	0 66	$e_{\{pp\} \sigma}$
-0.128071061169E+03	0 67	$f_{\{pp\} \sigma}$
-0.120457111706E+02	0 68	$\bar{f}_{\{pp\} \sigma}$
0.878497145096E+00	1 69	$g_{\{pp\} \sigma}$
-0.384410606818E+04	0 70	$e_{\{pp\} \pi}$
0.108361489944E+04	0 71	$f_{\{pp\} \pi}$
-0.439593271249E+02	0 72	$\bar{f}_{\{pp\} \pi}$
0.106970497340E+01	1 73	$g_{\{pp\} \pi}$
-0.112512341399E+05	0 74	$e_{\{sd\} \sigma}$
-0.115127280128E+03	0 75	$f_{\{sd\} \sigma}$
0.164270551053E+03	0 76	$\bar{f}_{\{sd\} \sigma}$
0.101368687502E+01	1 77	$g_{\{sd\} \sigma}$
-0.268382938574E+04	0 78	$e_{\{pd\} \sigma}$

-0.395327765604E+02	0 79	f_{pd sigma}
0.460782798868E+02	0 80	fbar_{pd sigma}
0.943864321191E+00	1 81	g_{pd sigma}
0.312284657830E+04	0 82	e_{pd pi}
-0.572706978713E+03	0 83	f_{pd pi}
0.736353859958E+01	0 84	fbar_{pd pi}
0.104142445979E+01	1 85	g_{pd pi}
0.120503301765E+04	0 86	e_{dd sigma}
-0.218261866122E+04	0 87	f_{dd sigma}
0.244415097237E+03	0 88	fbar_{dd sigma}
0.100373167180E+01	1 89	g_{pp sigma}
-0.293808504530E+03	0 90	e_{dd pi}
-0.194212572149E+03	0 91	f_{dd pi}
-0.404159492327E+02	0 92	fbar_{dd pi}
0.107950634834E+01	1 93	g_{pd pi}
-0.409235823075E+04	0 94	e_{dd delta}
-0.333290205710E+02	0 95	f_{dd delta}
0.467795241685E+02	0 96	fbar_{dd delta}
0.106179354689E+01	1 97	g_{dd delta}

A.6 Parameters for Lithium: Total Energies Only

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NN00000      (Old style Overlap Parameters)

Lithium  --

1             (One atom type in this file)

14.5   0.5    (RCUT and SCREENL for 1-1 interactions)

4        (Orbitals for atom 1)

6.941      (Atomic Weight of Atom 1)

1.0   0.0 0.0 (formal spd valence occupancy for atom 1)

0.109317137883E+01   0   1   Li-001 lambda (eq. 7)   Lithium

```

-0.465598794873E-01	0	2	Li-002 a_s	(eq. 9)	
0.524109259248E+01	0	3	Li-003 b_s	(eq. 9)	R_{cut} = 14.5
-0.260459510891E+02	0	4	Li-004 c_s	(eq. 9)	SCREENL = 0.5
0.715696670919E+02	0	5	Li-005 d_s	(eq. 9)	
0.230851130765E+00	0	6	Li-006 a_p	(eq. 9)	
0.375613847288E+01	0	7	Li-007 b_p	(eq. 9)	
-0.641175183644E+02	0	8	Li-008 c_p	(eq. 9)	
0.254613247459E+04	0	9	Li-009 d_p	(eq. 9)	
0.357253714922E+02	1	10	Li-010 a_t2g	(eq. 9)	
0.111264590042E-09	1	11	Li-011 b_t2g	(eq. 9)	
0.829097722099E-09	1	12	Li-012 c_t2g	(eq. 9)	
-0.256087133153E-09	1	13	Li-013 d_t2g	(eq. 9)	
0.115368476049E+02	1	14	Li-014 a_eg	(eq. 9)	
-0.456190670910E-09	1	15	Li-015 b_eg	(eq. 9)	
-0.789542852350E-09	1	16	Li-016 c_eg	(eq. 9)	
0.557502521177E-09	1	17	Li-017 d_eg	(eq. 9)	
0.108601383425E+02	0	18	Li-018 e_{ss sigma}	(eq. 10)	(Ham.)
-0.130809319205E+02	0	19	Li-019 f_{ss sigma}	(eq. 10)	(Ham.)
0.132113882627E+01	0	20	Li-020 fbar_{ss sigma}	(eq. 10)	(Ham.)
0.113980713134E+01	0	21	Li-021 g_{ss sigma}	(eq. 10)	(Ham.)
0.966386214420E+01	0	22	Li-022 e_{sp sigma}	(eq. 10)	(Ham.)
0.174340389314E+01	0	23	Li-023 f_{sp sigma}	(eq. 10)	(Ham.)
0.307230897061E+00	0	24	Li-024 fbar_{sp sigma}	(eq. 10)	(Ham.)
0.103302327032E+01	0	25	Li-025 g_{sp sigma}	(eq. 10)	(Ham.)
0.163947952782E+03	0	26	Li-026 e_{pp sigma}	(eq. 10)	(Ham.)
0.207147089858E+02	0	27	Li-027 f_{pp sigma}	(eq. 10)	(Ham.)
-0.824345820255E+01	0	28	Li-028 fbar_{pp sigma}	(eq. 10)	(Ham.)
0.101333576318E+01	0	29	Li-029 g_{pp sigma}	(eq. 10)	(Ham.)
0.133070906797E+02	0	30	Li-030 e_{pp pi}	(eq. 10)	(Ham.)
-0.528154918039E+01	0	31	Li-031 f_{pp pi}	(eq. 10)	(Ham.)

0.202240886520E+00	0	32	Li-032 $\bar{f}_{pp\ \pi}$	(eq. 10) (Ham.)
0.106815050984E+01	0	33	Li-033 $g_{pp\ \pi}$	(eq. 10) (Ham.)
-0.803610357079E-09	1	34	Li-034 $e_{sd\ \sigma}$	(eq. 10) (Ham.)
0.221270610122E-09	1	35	Li-035 $F_{sd\ \sigma}$	(eq. 10) (Ham.)
-0.736832101968E-09	1	36	Li-036 $\bar{f}_{sd\ \sigma}$	(eq. 10) (Ham.)
0.110857489522E+01	1	37	Li-037 $g_{sd\ \sigma}$	(eq. 10) (Ham.)
0.257632382462E-09	1	38	Li-038 $e_{pd\ \sigma}$	(eq. 10) (Ham.)
-0.706957636209E-09	1	39	Li-039 $f_{pd\ \sigma}$	(eq. 10) (Ham.)
0.295312523879E-09	1	40	Li-040 $\bar{f}_{pd\ \sigma}$	(eq. 10) (Ham.)
0.118238762680E+01	1	41	Li-041 $g_{pd\ \sigma}$	(eq. 10) (Ham.)
0.233066448652E-09	1	42	Li-042 $e_{pd\ \pi}$	(eq. 10) (Ham.)
-0.865483036457E-09	1	43	Li-043 $f_{pd\ \pi}$	(eq. 10) (Ham.)
0.808352915963E-09	1	44	Li-044 $\bar{f}_{pd\ \pi}$	(eq. 10) (Ham.)
0.111301989001E+01	1	45	Li-045 $g_{pd\ \pi}$	(eq. 10) (Ham.)
-0.240751734703E-09	1	46	Li-046 $e_{dd\ \sigma}$	(eq. 10) (Ham.)
0.100366788756E-09	1	47	Li-047 $f_{dd\ \sigma}$	(eq. 10) (Ham.)
0.129274918492E-09	1	48	Li-048 $\bar{f}_{dd\ \sigma}$	(eq. 10) (Ham.)
0.103425174744E+01	1	49	Li-049 $g_{dd\ \sigma}$	(eq. 10) (Ham.)
0.818134015984E-09	1	50	Li-050 $e_{dd\ \pi}$	(eq. 10) (Ham.)
0.265405021295E-09	1	51	Li-051 $f_{dd\ \pi}$	(eq. 10) (Ham.)
0.358414358701E-09	1	52	Li-052 $\bar{f}_{dd\ \pi}$	(eq. 10) (Ham.)
0.102466155482E+01	1	53	Li-053 $g_{dd\ \pi}$	(eq. 10) (Ham.)
-0.615251681044E-09	1	54	Li-054 $e_{dd\ \delta}$	(eq. 10) (Ham.)
0.341708376006E-09	1	55	Li-055 $f_{dd\ \delta}$	(eq. 10) (Ham.)
-0.540876116684E-09	1	56	Li-056 $\bar{f}_{dd\ \delta}$	(eq. 10) (Ham.)
0.101023078832E+01	1	57	Li-057 $g_{dd\ \delta}$	(eq. 10) (Ham.)
0.516266240767E+02	0	58	Li-058 $e_{ss\ \sigma}$	(eq. 10) (Ovr.)
-0.564441406010E+00	0	59	Li-059 $f_{ss\ \sigma}$	(eq. 10) (Ovr.)
-0.207708505812E+01	0	60	Li-060 $\bar{f}_{ss\ \sigma}$	(eq. 10) (Ovr.)
0.101416859849E+01	0	61	Li-061 $g_{ss\ \sigma}$	(eq. 10) (Ovr.)

-0.640127407723E+02	0	62	Li-062 e_{sp sigma}	(eq. 10) (Ovr.)
0.300604454625E+01	0	63	Li-063 f_{sp sigma}	(eq. 10) (Ovr.)
0.135097335877E+01	0	64	Li-064 fbar_{sp sigma}	(eq. 10) (Ovr.)
0.975378455928E+00	0	65	Li-065 g_{sp sigma}	(eq. 10) (Ovr.)
0.122693177397E+03	0	66	Li-066 e_{pp sigma}	(eq. 10) (Ovr.)
-0.593942253502E+01	0	67	Li-067 f_{pp sigma}	(eq. 10) (Ovr.)
-0.454885314860E+01	0	68	Li-068 fbar_{pp sigma}	(eq. 10) (Ovr.)
0.103215384025E+01	0	69	Li-069 g_{pp sigma}	(eq. 10) (Ovr.)
0.926236535858E+02	0	70	Li-070 e_{pp pi}	(eq. 10) (Ovr.)
0.252637100079E+01	0	71	Li-071 f_{pp pi}	(eq. 10) (Ovr.)
-0.297706008428E+01	0	72	Li-072 fbar_{pp pi}	(eq. 10) (Ovr.)
0.104372511417E+01	0	73	Li-073 g_{pp pi}	(eq. 10) (Ovr.)
0.813851939232E-09	1	74	Li-074 e_{sd sigma}	(eq. 10) (Ovr.)
-0.232655821638E-09	1	75	Li-075 f_{sd sigma}	(eq. 10) (Ovr.)
0.867127192065E-09	1	76	Li-076 fbar_{sd sigma}	(eq. 10) (Ovr.)
0.970482978604E+00	1	77	Li-077 g_{sd sigma}	(eq. 10) (Ovr.)
0.592417924033E-09	1	78	Li-078 e_{pd sigma}	(eq. 10) (Ovr.)
-0.295873323079E-09	1	79	Li-079 f_{pd sigma}	(eq. 10) (Ovr.)
0.360783461039E-09	1	80	Li-080 fbar_{pd sigma}	(eq. 10) (Ovr.)
0.107177011203E+01	1	81	Li-081 g_{pd sigma}	(eq. 10) (Ovr.)
-0.246480884019E-09	1	82	Li-082 e_{pd pi}	(eq. 10) (Ovr.)
-0.367815692732E-09	1	83	Li-083 f_{pd pi}	(eq. 10) (Ovr.)
-0.393422108846E-09	1	84	Li-084 fbar_{pd pi}	(eq. 10) (Ovr.)
0.104665362872E+01	1	85	Li-085 g_{pd pi}	(eq. 10) (Ovr.)
-0.549685570050E-09	1	86	Li-086 e_{dd sigma}	(eq. 10) (Ovr.)
-0.598862233065E-09	1	87	Li-087 f_{dd sigma}	(eq. 10) (Ovr.)
0.152052482205E-09	1	88	Li-088 fbar_{dd sigma}	(eq. 10) (Ovr.)
0.105778397157E+01	1	89	Li-089 g_{dd sigma}	(eq. 10) (Ovr.)
-0.360306391364E-09	1	90	Li-090 e_{dd pi}	(eq. 10) (Ovr.)
0.146211130748E-09	1	91	Li-091 f_{dd pi}	(eq. 10) (Ovr.)

-0.147743890508E-09	1	92	Li-092 fbar_{pp pi}	(eq. 10) (Ovr.)
0.973284750281E+00	1	93	Li-093 g_{dd pi}	(eq. 10) (Ovr.)
0.109300158641E-09	1	94	Li-094 e_{dd delta}	(eq. 10) (Ovr.)
-0.170779535190E-09	1	95	Li-095 f_{dd delta}	(eq. 10) (Ovr.)
0.107384782055E-09	1	96	Li-096 fbar_{dd delta}	(eq. 10) (Ovr.)
0.103225302505E+01	1	97	Li-097 g_{dd delta}	(eq. 10) (Ovr.)

A.7 Parameters for Lithium: Bands Only

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NN00000          (Old style Overlap Parameters)

Lithium  --

1                (One atom type in this file)

16.5   0.5       (RCUT and SCREENL for 1-1 interactions)

9                (Orbitals for atom 1)

6.941           (Atomic Weight of Atom 1)

1.0   0.0 0.0    (formal spd valence occupancy for atom 1)

  0.105395474179E+01  0  1  Li-001 lambda  (ta}  (eq. 10) (Ovr.)
-0.916047958852E+00  0  2  Li-002 A_s      (ta}  (eq. 10) (Ovr.)
  0.665914906266E+01  0  3  Li-003 b_s      (ta}  (eq. 10) (Ovr.)
-0.668095884590E+01  0  4  Li-004 c_s      (ta}  (eq. 10) (Ovr.)
-0.105349904347E+03  0  5  Li-005 d_s      (ta}  (eq. 10) (Ovr.)
-0.835228678346E+00  0  6  Li-006 a_p      (ta}  (eq. 10) (Ovr.)
  0.122798393143E+01  0  7  Li-007 b_p      (ta}  (eq. 10) (Ovr.)
  0.903279415204E+02  0  8  Li-008 c_p      (ta}  (eq. 10) (Ovr.)
-0.285290211174E+03  0  9  Li-009 d_p      (ta}  (eq. 10) (Ovr.)
-0.450787625714E+00  0 10  Li-010 a_t2g    (ta}  (eq. 10) (Ovr.)
  0.127783856216E+02  0 11  Li-011 b_t2g    (ta}  (eq. 10) (Ovr.)
-0.105544014058E+03  0 12  Li-012 c_t2g    (ta}  (eq. 10) (Ovr.)
  0.888166444251E+03  0 13  Li-013 d_t2g    (ta}  (eq. 10) (Ovr.)
  0.352637762782E+00  0 14  Li-014 a_eg     (ta}  (eq. 10) (Ovr.)
  0.180211739563E+01  0 15  Li-015 b_eg     (ta}  (eq. 10) (Ovr.)

```

-0.148280563894E+03	0 16	Li-016 c_eg (ta}	(eq. 10) (Ovr.)
0.754297753452E+03	0 17	Li-017 d_eg (ta}	(eq. 10) (Ovr.)
-0.882684852957E+03	0 18	Li-018 e_{ss sigta}	(eq. 10) (Ovr.)
0.484962042524E+03	0 19	Li-019 f_{ss sigta}	(eq. 10) (Ovr.)
-0.711980575713E+02	0 20	Li-020 fbar_{ss ta}	(eq. 10) (Ovr.)
0.119404002073E+01	0 21	Li-021 g_{ss sigta}	(eq. 10) (Ovr.)
0.493238760469E+03	0 22	Li-022 e_{sp sigta}	(eq. 10) (Ovr.)
-0.722148919340E+02	0 23	Li-023 f_{sp sigta}	(eq. 10) (Ovr.)
-0.941495202163E+01	0 24	Li-024 fbar_{sp ta}	(eq. 10) (Ovr.)
0.112825761856E+01	0 25	Li-025 g_{sp sigta}	(eq. 10) (Ovr.)
-0.110008157670E+06	0 26	Li-026 e_{pp sigta}	(eq. 10) (Ovr.)
-0.341064078209E+03	0 27	Li-027 f_{pp sigta}	(eq. 10) (Ovr.)
0.390781344206E+04	0 28	Li-028 fbar_{pp ta}	(eq. 10) (Ovr.)
0.140235719537E+01	0 29	Li-029 g_{pp sigta}	(eq. 10) (Ovr.)
-0.424315891337E+02	0 30	Li-030 e_{pp pi}ta}	(eq. 10) (Ovr.)
-0.246184709253E+01	0 31	Li-031 f_{pp pi}ta}	(eq. 10) (Ovr.)
0.525784615472E+00	0 32	Li-032 fbar_{pp ta}	(eq. 10) (Ovr.)
0.108133368823E+01	1 33	Li-033 g_{pp pi}ta}	(eq. 10) (Ovr.)
-0.854355566245E+03	0 34	Li-034 e_{sd sigta}	(eq. 10) (Ovr.)
0.213561875922E+03	0 35	Li-035 f_{sd sigta}	(eq. 10) (Ovr.)
-0.762726962984E+01	0 36	Li-036 fbar_{sd ta}	(eq. 10) (Ovr.)
0.106769962670E+01	0 37	Li-037 g_{sd sigta}	(eq. 10) (Ovr.)
0.217497734692E+04	0 38	Li-038 e_{pd sigta}	(eq. 10) (Ovr.)
-0.390128514289E+03	0 39	Li-039 f_{pd sigta}	(eq. 10) (Ovr.)
-0.502369400591E+01	0 40	Li-040 fbar_{pd ta}	(eq. 10) (Ovr.)
0.112094009055E+01	0 41	Li-041 g_{pd sigta}	(eq. 10) (Ovr.)
0.164305753042E+04	0 42	Li-042 e_{pd pi}ta}	(eq. 10) (Ovr.)
-0.814863970897E+03	0 43	Li-043 f_{pd pi}ta}	(eq. 10) (Ovr.)
0.104067342222E+03	0 44	Li-044 fbar_{pd ta}	(eq. 10) (Ovr.)
0.119138459308E+01	0 45	Li-045 g_{pd pi}ta}	(eq. 10) (Ovr.)

-0.181284827574E+03	0 46	Li-046 e_{dd sigta}	(eq. 10) (Ovr.)
0.117979583327E+03	0 47	Li-047 f_{dd sigta}	(eq. 10) (Ovr.)
-0.154838710655E+02	0 48	Li-048 fbar_{dd ta}	(eq. 10) (Ovr.)
0.103425174744E+01	1 49	Li-049 g_{dd sigta}	(eq. 10) (Ovr.)
-0.134408650441E+03	0 50	Li-050 e_{dd pi}ta}	(eq. 10) (Ovr.)
0.155317628238E+02	0 51	Li-051 f_{dd pi}ta}	(eq. 10) (Ovr.)
0.278344300928E+01	0 52	Li-052 fbar_{dd ta}	(eq. 10) (Ovr.)
0.102466155482E+01	1 53	Li-053 g_{dd pi}ta}	(eq. 10) (Ovr.)
0.172687998973E+04	0 54	Li-054 e_{dd delta}	(eq. 10) (Ovr.)
0.392173579467E+03	0 55	Li-055 f_{dd delta}	(eq. 10) (Ovr.)
-0.128094944007E+03	0 56	Li-056 fbar_{dd ta}	(eq. 10) (Ovr.)
0.123459162986E+01	0 57	Li-057 g_{dd delta}	(eq. 10) (Ovr.)
-0.241562580582E+04	0 58	Li-058 e_{ss sigta}	(eq. 10) (Ovr.)
0.530247105755E+03	0 59	Li-059 f_{ss sigta}	(eq. 10) (Ovr.)
0.653479225404E+01	0 60	Li-060 fbar_{ss ta}	(eq. 10) (Ovr.)
0.127123766907E+01	0 61	Li-061 g_{ss sigta}	(eq. 10) (Ovr.)
0.139048844674E+03	0 62	Li-062 e_{sp sigta}	(eq. 10) (Ovr.)
0.472112091336E+02	0 63	Li-063 f_{sp sigta}	(eq. 10) (Ovr.)
0.939544697169E+01	0 64	Li-064 fbar_{sp ta}	(eq. 10) (Ovr.)
0.123744896351E+01	0 65	Li-065 g_{sp sigta}	(eq. 10) (Ovr.)
0.188037810997E+05	0 66	Li-066 e_{pp sigta}	(eq. 10) (Ovr.)
-0.193245963435E+04	0 67	Li-067 f_{pp sigta}	(eq. 10) (Ovr.)
-0.836249196647E+03	0 68	Li-068 fbar_{pp ta}	(eq. 10) (Ovr.)
0.142691194146E+01	0 69	Li-069 g_{pp sigta}	(eq. 10) (Ovr.)
0.558972471280E+02	0 70	Li-070 e_{pp pi}ta}	(eq. 10) (Ovr.)
0.939774685262E+02	0 71	Li-071 f_{pp pi}ta}	(eq. 10) (Ovr.)
-0.171151857017E+02	0 72	Li-072 fbar_{pp ta}	(eq. 10) (Ovr.)
0.111455380770E+01	0 73	Li-073 g_{pp pi}ta}	(eq. 10) (Ovr.)
0.882037830983E+02	0 74	Li-074 e_{sd sigta}	(eq. 10) (Ovr.)
-0.276262394295E+02	0 75	Li-075 f_{sd sigta}	(eq. 10) (Ovr.)

0.167016477440E+01	0 76	Li-076 $\bar{f}_{sd\ \sigma}$	(eq. 10) (Ovr.)
0.885766123030E+00	0 77	Li-077 $g_{sd\ \sigma}$	(eq. 10) (Ovr.)
-0.269083995523E+03	0 78	Li-078 $e_{pd\ \sigma}$	(eq. 10) (Ovr.)
-0.225986697153E+03	0 79	Li-079 $f_{pd\ \sigma}$	(eq. 10) (Ovr.)
0.580891815233E+02	0 80	Li-080 $\bar{f}_{pd\ \sigma}$	(eq. 10) (Ovr.)
0.113338164309E+01	0 81	Li-081 $g_{pd\ \sigma}$	(eq. 10) (Ovr.)
-0.613077294280E+02	0 82	Li-082 $e_{pd\ \pi}$	(eq. 10) (Ovr.)
-0.928180422847E+01	0 83	Li-083 $f_{pd\ \pi}$	(eq. 10) (Ovr.)
0.182282418664E+01	0 84	Li-084 $\bar{f}_{pd\ \sigma}$	(eq. 10) (Ovr.)
0.104665362872E+01	1 85	Li-085 $g_{pd\ \pi}$	(eq. 10) (Ovr.)
0.295805918170E+03	0 86	Li-086 $e_{dd\ \sigma}$	(eq. 10) (Ovr.)
-0.138245886304E+03	0 87	Li-087 $f_{dd\ \sigma}$	(eq. 10) (Ovr.)
0.185536878842E+02	0 88	Li-088 $\bar{f}_{dd\ \sigma}$	(eq. 10) (Ovr.)
0.102617390802E+01	0 89	Li-089 $g_{dd\ \sigma}$	(eq. 10) (Ovr.)
-0.313464502066E+03	0 90	Li-090 $e_{dd\ \pi}$	(eq. 10) (Ovr.)
0.897709916350E+02	0 91	Li-091 $f_{dd\ \pi}$	(eq. 10) (Ovr.)
-0.847593243390E+01	0 92	Li-092 $\bar{f}_{pp\ \sigma}$	(eq. 10) (Ovr.)
0.100886946295E+01	0 93	Li-093 $g_{dd\ \pi}$	(eq. 10) (Ovr.)
0.746646876003E+03	0 94	Li-094 $e_{dd\ \Delta}$	(eq. 10) (Ovr.)
-0.218958646653E+03	0 95	Li-095 $f_{dd\ \Delta}$	(eq. 10) (Ovr.)
0.156233472198E+02	0 96	Li-096 $\bar{f}_{dd\ \sigma}$	(eq. 10) (Ovr.)
0.102862188249E+01	0 97	Li-097 $g_{dd\ \Delta}$	(eq. 10) (Ovr.)

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