MULTI-PURPOSE ELECTRONIC STRUCTURE PACKAGE

by

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A Dissertation
Submitted to the
Graduate Faculty
of
George Mason University
in Partial Fulfillment of
The Requirements for the Degree
of
Doctor of Philosophy
Computational Sciences and Informatics

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Date: 21 June 2010

Summer Semester 2010
George Mason University
Fairfax, VA

Multi-purpose Electronic Structure Package

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy at George Mason University

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DEDICATION

بسم الله الرحمن الرحيم

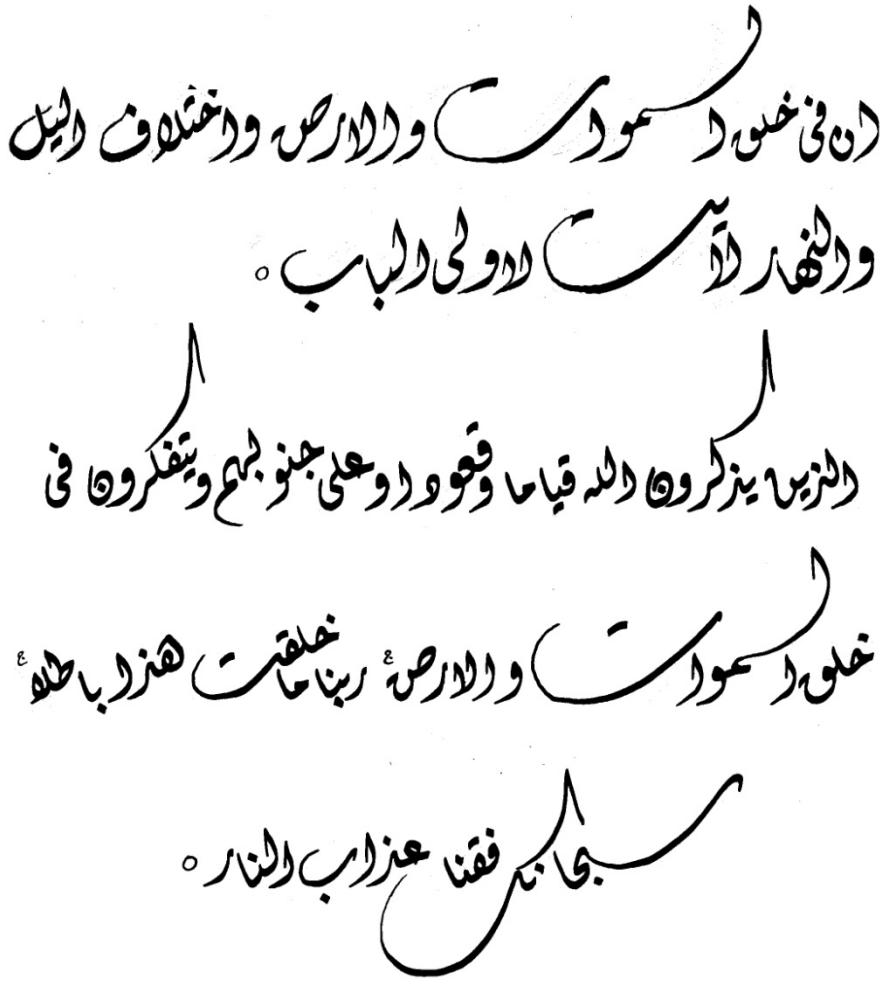
In the name of Allah[1], the Beneficent the Merciful.

[1] Allah is the proper name of God in Arabic, used alike by Arab Christians and Muslims.

ACKNOWLEDGEMENTS

From the bottom of my heart, I thank:

1. Allah the Glorious Most High. He created me and this universe - an opportunity for me to think, ponder, wonder about and then praise Him.



"Verily! In the creation of the heavens and the earth, and in the alternation of night and day, there are indeed signs for men of understanding. Those who remember Allah (always, and in prayers) standing, sitting, and lying down on their sides, and think deeply about the creation of the heavens and the earth, (saying): 'Our Lord! You have not created (all) this without purpose, glory to You! Give us salvation from the torment of the Fire'." [3:190-191] (Ameen)

2. Muhammad, peace be upon him, who commanded me to seek knowledge.

3. My parents, who were the first ones to teach me to read and write, always put my studies above their differences, spent long hours to teach me, spent their hard earned money on my education, and prayed for my success in public and in private, in this life and in the hereafter.

4. All of my teachers who have taught me everything that I know! I must have had more than a hundred formal teachers and countless informal teachers - each one of them incredibly important in my life.

5. My family who put up with me coming late at home, skipping weekend fun-time so that I can work on my dissertation, and missing out on all the fun that they could have had with the money that I spent on my PhD.

6. My siblings and cousins who look up to me as their eldest brother. (I constantly felt this pressure to keep getting higher degrees before they catch up - phew I am done now! The bar has just been raised.)

7. All those who have encouraged me to get PhD.

I remind myself of the saying of Rasoolullah, sallallahu alayhe wa sallam, something to the effect, 'The superiority of knowledge of Allah over all other knowledges is like that of Allah over His creation'.

And the verse of the Qur’an:

'O my Lord, increase me in knowledge.' [20:114]

And my final words are that all praise is due to Allah, the Lord and Cherisher of the worlds.

Table of Contents

PAGE

LIST OF TABLES ..... **ix**

LIST OF FIGURES ..... **x**

ABSTRACT ..... **xiv**

CHAPTER 1: INTRODUCTION **1**
- BACKGROUND 1

CHAPTER 2: ELECTRONIC STRUCTURE METHODS **3**
- BORN-OPPENHEIMER APPROXIMATION 3
- DENSITY FUNCTIONAL THEORY 3
- AUGMENTED PLANE WAVE (APW) 6
- LINEARIZED AUGMENTED PLANE WAVE (LAPW) 11
- NAVAL RESEARCH LAB TIGHT BINDING (NRL-TB) METHOD 12

CHAPTER 3: MULTI-PURPOSE ELECTRONIC STRUCTURE PACKAGE (MESP) **18**
- CAPABILITIES OVERVIEW 18
- AUTOMATION 19
- INTEGRATION 21
- HISTORY 21
- GRAPHICAL USER INTERFACE (GUI) 22
- AUTOMATIC RESULT EVALUATION 22
- PORTABLE DATA FORMAT 23
- GETTING STARTED 23
- USING A SAMPLE PROJECT 25
- CREATING A NEW PROJECT 29
- MESP LATTICE PARAMETER ESTIMATION 31
- MESP INTERACTIVE PLOTTING FACILITY 32

CHAPTER 4: APW WITH MESP **43**
- SUPPORTED CRYSTALLINE STRUCTURES FOR APW COMPUTATIONS 43
- INPUT FOR APW COMPUTATIONS 43
- RUNNING APW 44
- INSPECTING APW RESULTS 46
- SAMPLE COMPUTATIONS WITH COPPER 48

Sample Computations with Vanadium 51
Sample Computations with Titanium-Nickel (TiNi) 55
Ground State Crystalline Structure 64

CHAPTER 5: LAPW WITH MESP 66
Supported Crystalline Structures for LAPW Computations 66
Input for LAPW Computations 66
Running LAPW 67
Inspecting LAPW Results 69

CHAPTER 6: TBFIT WITH MESP 72
Supported Crystalline Structures for TBFIT Computations 72
Input for TBFIT Computations 72
Running TBFIT 72
Inspecting TBFIT Results 74

CHAPTER 7: STATIC WITH MESP 76
Supported Crystalline Structures for STATIC Computations 76
Input for STATIC Computations 76
Input to STATIC Program 77
Running STATIC 77
Inspecting STATIC Results 80
Sample Computations with Copper 83
Sample Computations with Vanadium 86
Sample Computations with Niobium 89

CHAPTER 8: TBMD WITH MESP 93
Supported Crystalline Structures for TBMD Computations 93
Input for TBMD Computations 93
Running TBMD 94
Inspecting TBMD Results 94
Sample Computations with Copper 96
Sample Computations with Vanadium 98

CHAPTER 9: TIGHT-BINDING FIT FOR POTASSIUM 101
Ground State 102
Lattice Parameter 104
Elastic Constants 105
Energy Bands 108
Density of States 110
BCC Phonon Frequencies 111
Tight-Binding Molecular Dynamics 112

CHAPTER 10: COMPUTATIONS WITH MAGNESIUM OXIDE (MGO) 114
Structural Comparison 114
Comparison with Other Studies 119
Band Structures 122

CHAPTER 11: HEAVY METALS 126
LAWRENCIUM 126
RUTHERFORDIUM 132
DUBNIUM 138
BIBLIOGRAPHY 145

List of Tables

Table **Page**
Table 1 Lattice Parameters and Bulk Moduli of Copper computed via APW..... 49
Table 2 Lattice Parameters and Bulk Moduli of Vanadium computed via APW..... 53
Table 3 Lattice Parameters and Bulk Moduli of TiNi computed via APW..... 65
Table 4 Lattice Parameters and Bulk Moduliof copper computed via STATIC 84
Table 5 Lattice Parameters and Bulk Moduli of Vanadium computed via STATIC..... 87
Table 6 Lattice Parameters and Bulk Moduli of Niobium computed via STATIC..... 91
Table 7 RMS errors related to parameters fit for Potassium 102
Table 8 Comparison of elastic constants and bulk modulus computed via STATIC with the experimental results 107
Table 9 Phonon frequencies of BCC Potassium computed via STATIC using the fitted parameters..... 111
Table 10 Band gaps of MgO at Γpoint..... 123
Table 11 Density of States (DOS) decomposition of Lawrencium at fermi level..... 131
Table 12 Density of States (DOS) decomposition of Rutherfordium at fermi level 137
Table 13 Density of States (DOS) decomposition of Dubnium at fermi level..... 143

List of Figures

Figure **Page**

Figure 1: Multi-purpose Electronic Structure Package (MESP)..... 19
Figure 2: A view of the application, showing various areas for windows..... 24
Figure 3: Opening a closed sub-window. 25
Figure 5: First screen of New Project Wizard. 26
Figure 6: Second screen of the New Project Wizard. 28
Figure 7: Newly created project shown in the Explorer area of the application..... 29
Figure 8: Creating a new project..... 30
Figure 9: Selecting an element for the project. 30
Figure 10: Selecting a name and a project directory for the newly created project..... 31
Figure 11: Click on the 'Plot' option to plot the curve. 33
Figure 12: A total energy curve being displayed in the 'Editor' area. 33
Figure 13: Editing XML data of the plot file. 34
Figure 14: Two plot files displayed together in a plot. 35
Figure 15: Selecting a region zooms in..... 36
Figure 16: Hovering mouse over a point displays data values. 37
Figure 19: Resetting zoom to default. 40
Figure 20: A combined plot of BCC and FCC total energy versus volume. 41
Figure 21: Displaying a .png file in 'Editor' area. 42
Figure 22: Click on the 'Compute' option of the pop-up menu. 45
Figure 23: Editing apw.mesp file with MESP editor. 46
Figure 24: Computations results directory structures. 47
Figure 25: APW calculation results 48
Figure 26: Volume vs. Total Energy for FCC and BCC structures of Copper 49
Figure 27: Energy bands of Copper at equilibrium parameter of FCC structure..... 50
Figure 28: Cumulative density of states for Copper at equilibrium parameter for FCC structure..... 51
Figure 29: Total Energy vs. Volume for FCC and BCC structures of Vanadium 52
Figure 30: Total Energy as a function of lattice parameter for Vanadium in BCC structure as computed by APW program. 53
Figure 31: Band energies for BCC Vanadium at equilibrium lattice parameter..... 54
Figure 32: Density of states of BCC Vanadium at equilbrium lattice parameter. 55

Figure 33: Total Energy vs. Lattice Parameter of Titanium-Nickel (TiNi) in Sodium-Chloride (NaCl) crystalline structure. 56
Figure 34: The band structure of NaCl crystalline structure Titanium-Nickel (TiNi) at equilibrium lattice parameter. 57
Figure 35: Density of States of NaCl crystalline structure Titanium-Nickel (TiNi) at equilibrium parameter. 58
Figure 36: Density of States of NaCl crystalline structure Titanium-Nickel (TiNi) at equilibrium parameter. 59
Figure 37: Density of States of NaCl crystalline structure Titanium-Nickel (TiNi) at equilibrium parameter. 60
Figure 38: Total Energy vs. Lattice Parameter of Cesium Chlordie (CsCl) crystalline structure of Titanium-Nickel (TiNi). 61
Figure 39: Band Structure of Cesium-Chloride (CsCl) crystalline structure Titanium-Chloride (TiNi) at equilibrium lattice parameter. The horizontal line shows the fermi level. 62
Figure 40: Density of States (DOS) of Cesium-Chloride (CsCl) crystalline structure Titanium-Chloride (TiNi) at equilibrium lattice parameter. 63
Figure 41: Density of States of Cesium-Chloride (CsCl) crystalline structure Titanium-Chloride (TiNi) at equilibrium lattice parameter. The vertical line shows the fermi level. 64
Figure 42: Comparison of total energy vs. volume of NaCl and CsCl structures. 65
Figure 43: Click on the 'Compute' option of the pop-up menu. 67
Figure 44: Editing lapw.mesp file with MESP editor. 68
Figure 45: Computations results directory structures. 70
Figure 46: Click on the 'Compute' option of the pop-up menu. 73
Figure 47: Editing tbfit.mesp file with MESP editor. 74
Figure 48: Computations results directory structures. 75
Figure 49: static.mesp in MESP Editor. The blank fields would force MESP to estimate the values by consulting it's internal database. 78
Figure 50: Select the ~/.mesp/Vanadium/mespproject/v_par file. 79
Figure 51: To run STATIC, right click on static.mesp and click on 'Compute'. 80
Figure 52: Computations results directory structures. 81
Figure 53: Various directories inside a crystalline structure directory. 82
Figure 54: Displaying a .png file in 'Editor' area. 83
Figure 55: Volume vs. Total Energy for FCC and BCC structures of Copper 84
Figure 56: Band energies of FCC Copper. The vertical axis represents the energy in Rydbergs. The horizontal axis has points of high symmetry in a BCC crystalline structure 85
Figure 57: Densities of State (DOS) plot of FCC Copper at equilibrium lattice parameter. The horizontal axis represents the total energy in Rydbergs and the vertical axis is the density of states. 86
Figure 58: Total Energy vs. Volume for FCC and BCC structures of Vanadium 87

Figure 59: Band energies of BCC Vanadium at equilibrium lattice parameter. The horizontal pink line represents the fermi energy. The vertical axis represents the energy in Rydbergs. The horizontal axis has points of high symmetry in a BCC crystalline structure..... 88
Figure 60: Densities of State (DOS) plot of BCC Vanadium at equilibrium lattice parameter. The horizontal axis represents the total energy in Rydbergs and the vertical axis is the density of states. The green vertical line represents the fermi energy. 89
Figure 61: Total energies of, top to bottom, diamond, simple cubic, FCC, and BCC crystalline structures. The plot represents the Birch fit to original data. 90
Figure 62: Band energies of BCC Niobium at equilibrium lattice parameter. The horizontal pink line represents the fermi energy. The vertical axis represents the energy in Rydbergs. The horizontal axis has points of high symmetry in a BCC crystalline structure..... 91
Figure 63: Densities of State (DOS) plot of BCC Niobium at equilibrium lattice parameter. The horizontal axis represents the total energy in Rydbergs and the vertical axis is the density of states. The green vertical line represents the fermi energy. 92
Figure 64: Right click on the .mesp file and click on 'Compute' menu option on the pop-up menu..... 94
Figure 65: Computations results directory structures. 95
Figure 66: Various directories inside a crystalline structure directory and a sample temperature variation plot. 96
Figure 67: Each plot represents a different starting temperature. 97
Figure 68: Each plot represents a different starting temperature. 98
Figure 69: Each plot represents a different starting temperature. 99
Figure 70: Each plot represents a different starting temperature 100
Figure 71: Total energy computed via APW technique..... 101
Figure 72: Total energy vs. volume of various crystalline structures using newly-found tight-binding parameters of potassium..... 103
Figure 73: A closeup of total energy versus volume to see the difference in energy. 104
Figure 74: Total energy plot as a function of BCC lattice parameter. 105
Figure 75: Energy as a function of Orthorhombic strain displacement for the BCC lattice. 106
Figure 76: Energy as a function of displacement due to monoclinic strain on BCC K structure to determine C_{44}. 107
Figure 77: Energy bands of K in BCC structure using tight-binding parameters..... 108
Figure 78: Energy bands of K in BCC structure via the APW technique..... 109
Figure 79: Density of States (DOS) of Potassium in BCC structure using tight-binding parameters 110
Figure 80: Density of States (DOS) of Potassium in BCC structure via APW technique. 111
Figure 81: Temperature variations from different starting temperatures for BCC Potassium at 9.52 bohr fixed lattice parameter (fixed volume). 113
Figure 82: Energy as a function of volume for NaCl and CsCl structures of MgO. 115

Figure 83: Enthalpy as a function of Pressure for NaCl and CsCl structures of MgO. .. 116
Figure 84: Pressure as a function of volume for the two structures. The horizontal line shows the transition pressure of 126 GPa. 117
Figure 85: A close up of pressure as a function of volume for the two structures. The horizontal line shows the transition pressure of 126.25 GPa. 118
Figure 86: Comparison of phase transition with Mehl et. al. [Mehl] study with LAPW technique. 120
Figure 87: Comparison of Enthalpies by Karki et. al. [Karki]..... 121
Figure 88: Band structure of MgO in CsCl crystalline structure at equilibrium lattice parameter of 4.91 bohr. 122
Figure 90: Density of States of MgO with Magnesium contributions. 124
Figure 91: Density of States as with Oxygen contributions. 125
Figure 92: Total Energy vs. Volume..... 127
Figure 93: Total Energy vs. Lattice Parameter 128
Figure 94: Band structure of Lr at equilibrium lattice parameter. 129
Figure 95: Density of states of Lr FCC..... 130
Figure 96: A close-up of the DOS towards the higher energy window shows the details of the DOS structure for FCC Lr..... 131
Figure 97: Total Energy vs. Volume..... 133
Figure 98: Total Energy vs. Lattice Parameter 134
Figure 99: Band structure of Rf at FCC equilibrium lattice parameter. 135
Figure 100: Density of states of Rf at FCC equilibrium parameter. 136
Figure 101: Higher energy density of states of FCC Rf. 137
Figure 102: Total Energy vs. Volume..... 139
Figure 103: Total Energy vs. Lattice Parameter 140
Figure 104: Band structure of Db at BCC equilibrium lattice parameter. 141
Figure 105: Density of states at BCC equilibrium parameter of Db..... 142
Figure 106: A close-up of higher energy density of states of BCC Db. 143

ABSTRACT

MULTI-PURPOSE ELECTRONIC STRUCTURE PACKAGE

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This dissertation uses the following well-known scientific computation programs:

- Augmented Plane Wave (APW) Method
- Linearized Augmented Plane Wave (LAPW) Method
- Naval Research Laboratory's Tight Binding Method (NRL-TB)
- Fitting Code To Find Tight-Binding Parameters (TBFIT)
- Scalable Tight Binding Total Energy Evaluation Code (STATIC)
- Tight Binding Molecular Dynamics. (TBMD)

The output of some of these programs is often fed as input to other programs, sometimes by using some other programs. This dissertation first builds a tool that automates the entire process, provides a Graphical User Interface (GUI), facilitates storing the data in a reusable format, and provides means to view relevant information in plotted forms.

All of the programs listed above are developed over past decades by various scientists at Naval Research Laboratory (NRL) using FORTRAN. This dissertation utilizes the time and effort investment already made and builds on it to provide an integrated, automated, and user-friendly software with a GUI. This software also has an integrated plotting component to it to display various charts.

The results of a program are evaluated. The output is automatically scanned to get key quantities. These key quantities are fed to the next program as input. In case the previous program reports any errors, those errors are reported accordingly to the user and any further processing of computations is interrupted.

Some of the programs mentioned above have an interactive interface. Thus a user has to answer a number of questions in order to initiate a calculation. If the user makes a mistake or wishes to alter one of the responses provided to the program's questions, the user has to cancel the calculation and start afresh. This software is capable to store all the specifications regarding a calculation. The software is able to read these specifications and start the calculation. This provides the user means to alter input at will and also means to store the input as reference for later comparisons.

Using this newly created tool called Multipurpose Electronic Structure Package, the following research was conducted:

- A new set of Tight-Binding parameters for Potassium are produced by fitting tight-binding parameter functions through results produced by APW, a first-principles technique. These parameters are then used to validate against the APW computational results and also to get additional quantities. They are also used to

ensure that they would perform adequately in a Tight-Binding Molecular Dynamics (TBMD) setting.

- A new study on Magnesium Oxide (MgO) is presented based on the APW first-principles technique. It computes total energy and enthalpy under varying pressure and estimates a pressure of 126 GPa when Mgo transitions from NaCl crystalline structure to CsCl crystalline structure. A limited comparative study is also provided.
- First-principles based APW is again used to study three heavy metals that don't exist in nature and are created in laboratories: Lawrencium, Rutherfordium, and Dubnium. The ground-state crystalline structure, lattice parameters, band energies, density of states, and ferromagnetism are discussed. ,

Chapter 1: Introduction

Background

This dissertation first creates a Multi-purpose Electronic Structure Package (MESP) to utilize existing computational materials science tools in tandem to search for new materials, or perform calculations on known materials. These tools, based on density functional theory, often referred to as the electronic structure methods, are used to determine electronic and mechanical properties of materials. For instance, by calculating the energy bands of a material, a determination is made as to whether a material is a metal, semiconductor, or an insulator. Calculations of density of electronic states (DOS) are used to interpret measurement of various crystallographic spectra. This combined with the DOS angular momentum components is used to connect with specific heat measurements and to evaluate the necessary conditions for superconductivity, and ferromagnetism to occur.

In addition, electronic structure methods are used to calculate the total energy of a given material and hence predict the stable structure, equilibrium lattice parameter and the elastic moduli.

The APW and LAPW tools are inherently slower than the NRL-TB method. The APW and LAPW methods are more precise but take longer to compute. The NRL-TB method

uses a reduced expansion of the wave function and hence takes less time to run for a comparable system, thus enabling the user to observe larger systems under varying temperature, pressure, or other conditions. By combining the two sets of programs, one can produce results within reasonable time-frame. MESP enables the user to do just that with minimal effort.

Also in this dissertation, the newly created tool, MESP, is used to:

- determine the tight-binding parameters of Potassium, validate results with first-principles based APW computation and compute other quantities of interest.
- determine the transition pressure of MgO, electronic band structure, density of states, and other quantities
- study Lawrencium, Rutherfordium, and Dubnium to determine their ground state crystalline structure, lattice parameter, electronic band structure, density of states, and any existence of ferromagnetism.

Chapter 2: Electronic Structure Methods

The Electronic Structure Methods presented here are mainly concerning a collection of computational techniques to compute the total energy and band structure of a solid. This collection of techniques was developed by several theoreticians.

Born-Oppenheimer Approximation

This approximation uses the fact that the nuclei are much heavier than the electrons and the electrons respond to any change in a much faster manner than the nuclei. Thus it approximates that the nuclei are stationary with respect to electrons. This can be thought of as if the material is at 0K. This approximation helps in solving the Schrödinger equation, as it separates the electronic motion from the ionic motion.

Density Functional Theory

After initial development of quantum mechanics, Slater and others laid the foundation by introducing the Energy Band Theory. However, this theory was supported by several others over the years. Kohn and others provided a firm foundation by introducing Density Functional Theory (DFT). DFT has two underlying theorems:

1. The total energy of an atomic system $E(\rho)$is a functional of the ground state electronic density ρ. Or,
    a. $E = E(\rho)$
    b. For a spin polarized system, this becomes

       $E = E(\rho\uparrow, \rho\downarrow)$
2. The ground state density is the density that minimizes $E(\rho)$.

With these two simple assumptions, the many body problem introduced by Slater is reduced to a one-body problem. According to DFT, the total energy of a system is written as:

$$E(\rho) = T(\rho) + E_{e-e}(\rho) + E_{e-n}(\rho) + E_{n-n}(\rho) + E_{xc}(\rho) \quad (1)$$

Where $T(\rho)$is the single particle kinetic energy computed by adding the one electron eigenvalues in the Schrödinger equation, $E_{e-e}(\rho)$is the electron to electron Coulomb interaction, $E_{e-n}(\rho)$represents the potential energy due to interaction between electrons and the nuclei of the atomic system, $E_{n-n}(\rho)$is the interaction between nuclei, and $E_{xc}(\rho)$is the exchange correlation energy, which is approximated – using Local Density Approximation (LDA) or Generalized Gradient Approximation (GGA).

This approach utilizes the Born-Oppenheimer Approximation.

In Electronic Structure Methods the Schrödinger equation is solved:

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

The wave function is expanded using a polynomial expansion:

$$\psi(r) = \sum_j a_j \phi_j(r) \quad (3)$$

This manifests itself in a system of linear equations for which eigenvalues are found. Much research has taken place in determining the form of ϕ. Some of the various methods of computing the electronic structure of a material are listed below:

Augmented Plane Wave (APW) method

This uses the Muffin-tin or full-potential form. The linearized methods include Linearized Augmented Plane Wave (LAPW) method and Linear Muffin-Tin Orbital (LMTO) methods.

Linearized Augmented Plane Wave (LAPW) method

This method uses a general potential removing the Muffin-tin approximation.

Atomic Sphere Approximation

This method includes Linear Muffin-Tin Orbitals (LMTO) and Augmented Spherical Waves (ASW).

Muffin-tin Orbitals method

KKR method

This method is based on multiple scattering theory.

Pseudopotential methods

This method freezes the core electrons and focuses on the outer electrons. It is also related to the Orthogonalized Plane Wave (OPW) method.

The APW and LAPW methods are used in the presented suite of programs.

Augmented Plane Wave (APW)

The Augmented Plane Wave (APW) software program is developed by Prof. Dimitrios A. Papaconstantopoulos and his collaborators Larry Boyer, Bary Klein and Brahim Akdim. This program is based on Energy Band Theory (EBT). Using this approach one may be able to predict the following properties of materials:

- determine if the material is a metal, semiconductor, or an insulator
- the stable crystal structure and the equilibrium lattice constant
- the bulk modulus
- the electron-phonon coupling needed in the theory f superconductivity
- whether the material exhibits ferromagnetism (Stoner criterion)
- various spectra, such as X-Ray, XPS, etc.
- potential function as an input to molecular dynamics

In the APW program as in other electronic structure methods the Schrödinger equation, equation (2) above, is solved. In this method the atoms in the crystal lattice are surrounded by touching spheres called muffin-tin spheres. The wavefunction has spherical harmonics form within the muffin-tin spheres around atoms and has a plane wave form outside those spheres. Thus ψwithin the spheres looks like:

$$\phi(r) = \sum_{lm} A_{lm} Y_{lm}(r) u_l(r, \varepsilon) \qquad (4)$$

where $A_{lm}$is determined by the boundary conditions at the muffin-tin sphere to assure the continuity of the wave function outside the muffin-tin spheres, where it has the form of a

plane wave. The crystal potential is a spherically symmetric function inside the spheres and constant outside the spheres. The plane wave expression looks like:

$$\phi(r) = \exp(ik.r) \quad (5)$$

Placing these wave functions into the Schrödinger equation yields a system of linear equations. Using techniques to find eigenvalues of that system solves the electronic structure problem and determines the energy bands, the density of states, and the total energy. The *k*-point meshes contain 89 points for FCC and 55 points for BCC structures, in the irreducible Brillouin zone, including the origin point. In all cases the Hedin-Lundqvist parameterization of the local density approximation (LDA) is used to support Density Functional Theory (DFT).

This technique is incorporated into the Self-Consistency Cycle. This cycle consists of steps:

- Make an initial guess of the charge density from superposition of atomic charge densities
- Solve Schrödinger equation to compute new charge densities separately for core and valence electrons
- Solve Poisson's equation to get a new potential
- Mix the old and new charge densities to repeat the cycle
- Terminate cycle until the electron charge density or total energy converges to within some tolerance criterion.

The APW program solves these equations repeatedly for various lattice parameters and crystalline structures yielding a relationship between lattice parameter and total energy. It

then continues to study this fundamental relationship to determine the aforementioned physical properties of the system.

The APW program works well for cubic materials but due to the Muffin-tin approximation lacks the necessary accuracy for open low symmetry crystal structures. However, the Muffin-tin APW program has one advantage over the LAPW program described below that has utilized group theory to block diagonalize the secular equation and therefore identifies its electron state with appropriate symmetry, i.e. at the center of the Brillioun zone: $\Gamma_1, \Gamma_{12}, \Gamma_{25}', \Gamma_{15}$etc.

APW is an interactive program. MESP takes options from the user, possibly store them in a file, and interacts with APW without further input from the user. MESP provides a range of lattice parameters, based on the approximate equilibrium lattice parameter provided by the user, or if omitted, estimated from experiment. For some of the input to APW that is material dependent an internal database of elemental information is consulted. MESP rounds off each evaluation of a lattice parameter to the nearest 0.1 bohr. After the total energy computation, MESP automatically computes the energy bands and density of states computations. It also converts the plots produced in Postscript (.ps) and Encapsulated Postscript (.eps) format to Portable Network Graphics (.png) format to facilitate viewing within MESP as well as on a common browser. MESP also produces .plot files of total energy in 'plots' directory to produce plots that can be interactively manipulated and superimposed with MESP environment.

The following properties can be obtained by using the APW package.

Energy Bands

The APW package computes in the First Brillouin Zone (BZ), the eigenvalues associated with its various points and directions.

Density of States (DOS)

The APW package computes the total Density of States (DOS) for the given material and also calculates the angular momentum components of the DOS (s, p, d, eg, t2g, and f).

McMillan Theory of Superconductivity

The temperature at which a material transitions into a superconducting material is given by:

$$T_c = \frac{\theta_D}{1.4} \exp \frac{-1.04(1+\lambda)}{\lambda - \mu^* - 0.2\lambda\mu^*}$$

The parameter $\mu^*$is called the Coulomb pseudopotential and has a value of 0.13 for transition metals and 0.1 for simple metals. θ_D is the Debye temperature.

Stoner Criterion of Ferromagnetism

The Stoner criterion is given by:

$$I_F N(E_F) > 1$$

I_F is evaluated using the l-components of Density of States (DOS) and the APW radial wavefunctions. $N(E_F)$ is the Density of States (DOS) at the Fermi Level (E_F). The material is ferromagnetic if the above criterion is satisfied.

In the APW package, it is computed by the program ston.f

Electron Phonon Coupling

The electron phonon coupling parameter is given by:

$$\lambda = \frac{\eta}{M<\omega^2>}$$

$\eta$is the Hopfield parameter and is calculated in the so-called rigid muffin-tin approximation of Gaspari-Gyorffy and Papaconstantopoulos et. al.

In the APW package, it is computed by the gyon.f program.

The parameter $<\omega^2>$ may be computed as:

$$<\omega^2> = \frac{1}{2}\theta_D^2$$

where $\theta_D$is the Debye temperature.

Specific Heat Capacity

Specific Heat Capacity is given by:

$$C = \gamma T + AT^3$$

where $\gamma T$is the electronic and $AT^3$is the lattice contribution.γ is given by:

$$\gamma = 0.1734(1 + \lambda)N(E_F)$$

$N(E_F)$ is states / Ry per atom for both spins and is expressed in units mJ/mol-deg^2.

Without the mass enhancement factor $(1 + \lambda)$ the value ofγshould be smaller than in the experiment.

Rigid Band Prediction

Given the Fermi level of an element, the Fermi level on a nearby element can be predicted by looking at the output of the DOS and moving E_F to correspond to the appropriate number of valence electrons.

Bulk Modulus

Bulk Modulus is given by:

$$K = -V\frac{\partial P}{\partial V} = -V\frac{\partial^2 E}{\partial V^2}$$

where P is pressure, E is total energy, and V is volume. It measures the response in pressure due to a change in relative volume.

Linearized Augmented Plane Wave (LAPW)

The Linearized Augmented Plane Wave (LAPW) method is an improved version of the APW program in which the muffin-tin (MT) approximation used in the APW method is removed. In the LAPW method the crystal potential (and the charge density) has a general form i.e. it is not spherically symmetric inside the MT spheres and it is not constant outside. The MT spheres are no longer required to touch each other. As a result the LAPW program can handle accurately materials of lower symmetry than cubic. The code used here was originally written by Henry Krakauer and David Singh. It was modified by Mike Mehl.

As with APW, MESP provides a range of lattice parameters to the LAPW program, based on the approximate equilibrium lattice parameter provided by the user, or if omitted,

estimated through experimental data. For some of the input to LAPW that is material dependent an internal database of elemental information is consulted. MESP rounds off each evaluation of a lattice parameter to the nearest 0.1 bohr. After the total energy computation, MESP automatically computes the band energy and elastic constants computations. It also converts the plots produced in Postscript (.ps) and Encapsulated Postscript (.eps) format to Portable Network Graphics (.png) format to facilitate viewing within MESP as well as on a common browser. MESP also produces .plot files of total energy in 'plots' directory to produce plots that can be interactively manipulated and superimposed in MESP integrated development environment.

Naval Research Lab Tight Binding (NRL-TB) Method

Density Functional Theory (DFT) gives the total energy in the form:

$$E[n(r)] = \sum_i f(\mu - \varepsilon_i)\varepsilon_i + F[n(r)] \quad (6)$$

where $n(\boldsymbol{r})$ is the electronic density, ε_i is the Kohn-Sham eigenvalue of the *i*th electronic state, μ is the chemical potential, and the sum is over all electronic states of the system.

In the NRL-TB method a shift is applied to the individual eigenvalues so that:

$$E[n(r)] = \sum_i f(\mu' - \varepsilon_i')\varepsilon_i' \quad (7)$$

where $\mu^i = \mu + V_o$, $\varepsilon_i' = \varepsilon + V_o$, and $V_o = \frac{F[n(r)]}{N_e}$. (8)

where N_e is the number of valence electrons in the system.

The onsite term for atom *i* is:

$$h_{i\alpha} = a_{i\alpha} + b_{i\alpha}\rho_i^{2/3} + c_{i\alpha}\rho_i^{4/3} + d_{i\alpha}\rho^2 \quad (9)$$

where $\rho_i = \sum_{j\neq i} \exp[-\lambda_{j\bar{i}}^1 R_{ij}] F_c(R_{ij})$ (10)

F_c is a smooth cutoff function, α is *s*, *p*, or *d*. Both the Hamiltonian and overlap parameters are estimated by the same functional form but with additional parameters:

$$P_\gamma(R) = (e_\gamma + f_\gamma R + \bar{f}_\gamma R^2)\exp[-g_\gamma^2 R] F_c(R) \quad (11)$$

where γ indicates the type of interaction (e.g. ssσ, $pd\pi$, etc.), *R* is the distance between the atoms and $\mathrm{F_c}(R)$ is a smooth cutoff function.

The parameters in equation 9-11, a total of ninety seven parameters, are determined using a nonlinear least squares method, by a fit to total energies and band structures computed using the muffin-tin potential augmented plane wave (APW) or the full-potential linearized augmented plane wave (APW) methods, for several lattice constants and crystal structures.

The code for Naval Research Laboratory Tight Binding Method (NRL-TB) was written by Mike Mehl, Dimitrios Papaconstantopoulos, Ron Cohen, Florian Kirchhoff and Noam Bernstein. The program has both orthogonal and non-orthogonal capabilities. The aim of this code is to recast the results of a first-principles calculation (such as the APW) in a tight-binding formalism which has the advantage of being computationally very fast and therefore capable of handling large systems and perform molecular dynamics simulations. The three main components of this software suite are briefly described below.

NRL-TB Fitting Code to Find Tight Binding Parameters

This code takes output from APW programs and computes the onsite Tight Binding parameters and the Slater Koster Two-Center integrals. The technique here is a least squares fitting of the APW eigenvalues at many k-points as well as the total energy values as a function of volume and structure. These parameters are used by NRL-STATIC and NRL-TBMD as input.

APW computes total energy for a given lattice parameter. As MESP asks APW to compute the total energies, it also makes sure that the output produced for each lattice parameter is changed to a form that NRL-TBFIT can understand and utilize. When a user asks MESP to fit parameters through the APW data, MESP first extrapolates the total energy curve produced by APW to at least accommodate 10% to the left and right of the equilibrium lattice parameter using the Birch-Murnaghan technique. It then creates symmetry files for the high symmetry points. These high symmetry points in Body Centered Cubic (BCC) are Gamma, H, P, and N and for Face Centered Cubic (FCC) are Gamma, L, X, W3, and W. When LAPW input is used, MESP also supplies the band information in the shape of a QLMT file to the fitting process. It then produces the input file for NRL-TBFIT. NRL-TBFIT gives an option of either fitting the band energy or not for a given lattice parameter. MESP starts fitting from the equilibrium lattice parameter using a user provided starting parameters. Once that is fitted, it uses the output of the fit as starting parameters for the next fit, which includes the total energy and the band information. MESP progressively includes closest adjacent points and gradually 'grows' the fit, saving the output in a separate directory for each run and using the output

parameters as input to the next step. As the fitting process progresses, the Root Mean Square (RMS) error increases for the total fit. The user can then make a decision suiting his or her circumstances better for a need of a wider curve or lesser RMS error.

NRL-TB STATIC

STATIC is a code which evaluates the total energy as well as the energy bands and the density of states (DOS) of a crystal or a cluster, using Tight-Binding parameters determined by the fitting code. A database of Tight-Binding Parameters is available for use with STATIC, or the code may be modified to use an alternative parametrization scheme. Both serial and parallel machines (using the Message Passing Interface (MPI) standard) can use the same source code.

STATIC was developed as part of the DoD-Parallel Tight-Binding Molecular Dynamics program of the Common HPC Software Support Initiative (CHSSI), under the Computational Chemistry and Materials Science (CCM) Computational Technology Area (CTA).

For a given system of atoms in a crystal or cluster, STATIC can be used to determine:

- Total energy vs. volume of the crystal structure
- Energy vs. c/a for Hexagonal Closed Packed (hcp) systems
- Bain path as a crystal transitions from BCC to FCC or vice versa
- Density of states for any structure
- Elastic constants
- Phonon frequencies for FCC, BCC, SC, Diamond (dia), and HCP structures

- Spin polarization of ferromagnetic and antiferromagnetic materials
- Vacancy Formation Energy

Elastic Constants

Elastic constants are computed by applying small strains while conserving volume and then computing the total energy. For $C_{11} - C_{12}$, the relationship is:

$$E(e_1) = E_0 + V(C_{11} - C_{12})e_1^2 + O[e_1^4] \quad (12)$$

where V is the volume of the structure. First the quantity$C_{11} - C_{12}$, known as the tetragonal shear modulus, is computed. Using the bulk modulus computed from the total energy plot for various lattice parameters, we get:

$$B = \frac{1}{3}(C_{11} + 2C_{12}) \quad (13)$$

where B is the Bulk modulus. Solving equations 12 and 13 gives us the values for elastic constants $C_{11}$and C_{12}.

For C_{44}, another computation is performed by varying the strain. A fit of the curve for the following equation is used:

$$E(e_6) = E_0 + \tfrac{1}{2}VC_{44}e_6^2 + O[e_6^4] \quad (14)$$

Vacancy Formation Energy

A supercell method is employed to compute the vacancy formation energy [Mehl1996]. The central atom of a 125 atom supercell is removed while the remaining 124 atoms are allowed to relax. The large supercell allows eliminating vacancy to vacancy interaction.

Total energy for 125 and 124 atoms is computed and used in the following equation to get vacancy formation energy.

$$E_{vacancy} = E_{(N-1)} - \frac{(N-1)}{N} E_N \quad (15)$$

where N is the total number of atoms (in this case 125).

NRL-TB Molecular Dynamics

NRL-TBMD is a code for doing molecular dynamics simulations on massively parallel computers.

NRL-TBMD is developed as part of the CHSSI CCM-3 project entitled DoD-Parallel Tight-Binding Molecular Dynamics, under the auspices of the DoD HPCMO as a part of the Computational Chemistry and Materials Science (CCM) CTA's contribution to the Common HPC Software Support Initiative (CHSSI).

The main features of this code are:

- Quantum Mechanical description of the inter-atomic interactions using the tight-binding approximation
- Support for metallic and non-metallic systems
- Non-orthogonal tight-binding models
- s, p and d orbitals
- Electronic structure calculation using $O(N^3)$ or $O(N^2)$ methods
- Scalable and portable code

Chapter 3: Multi-purpose Electronic Structure Package (MESP)

Following is a brief synopsis of the various features of the aforementioned programs that are utilized by MESP to calculate total energies.

Capabilities Overview

MESP uses the APW program to compute the following for the monoatomic in Simple Cubic (SC), Body Centered Cubic (BCC), and Face Centered Cubic (FCC) crystalline structures and for the diatomic structures NaCl and CsCl:

- Total Energy
- Fit the total energy values to find the equilibrium lattice parameter
- Computes the band structure and density of states (discussed in chapter 4)

MESP computes the same quantities as above using LAPW and in addition it can also compute elastic constants of Face Centered Cubic (FCC) and Body Centered Cubic (BCC) crystalline structures.

MESP is capable of taking the output of the APW program for monoatomic elements and using TBFIT iteratively fit parameters to the eigenvalues and total energy quantities computed in the APW calculation.

It also uses the fitted parameters to run TB-STATIC program to:

- Compute Total Energy
- Fit the total energy values to find the equilibrium lattice parameter
- Find the Bulk's modulus
- Compute Total Energy as a function of displacement squared to compute elastic constants.
- Vacancy formation energy
- MESP can also use the parameters to run NRL-TBMD program.

A screenshot of the product follows:

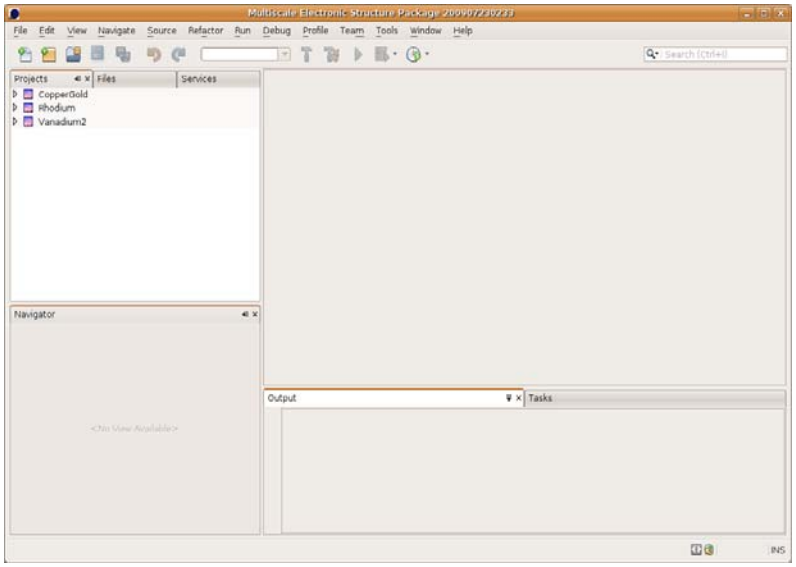

Figure 1: Multi-purpose Electronic Structure Package (MESP).

Automation

MESP automates various aspects of the programs that it uses. These automations are discussed below:

APW

Currently, APW takes input interactively. MESP eliminates the need for interaction at run-time. When the user creates a new MESP project, it presents the periodic table to the user to select elements. For each of the elements, MESP consults its built-in database to access the following quantities during various phases of the computation:

- Atomic number
- Atomic radius
- Periodic table group
- Valence electrons in s, p, d, & f orbitals.
- Experimental lattice parameter for either BCC or FCC crystalline structure.

MESP stores the element selection information along with the project information. When a user does not specify lattice parameter for a computation, MESP tries to look for the experimental value. If it cannot find an experimental lattice parameter value for a crystalline structure, it then estimates the lattice parameter of the requested crystalline structure from the given experimental lattice parameter for the other crystalline structure. In the rare incident where experimental values are not available, MESP resorts to estimating the lattice parameter from the atomic radius.

LAPW

In case a user does not specify an initial charge density file (CDN1) for the LAPW computation, MESP automatically creates one by running APW for the smallest lattice parameter. It then uses that charge density file to initiate the LAPW computation.

Given the atomic number, MESP can find out the core states to be used in the LAPW computation. Given a crystalline structure, MESP generates the primitive lattice vectors for the crystal to be used in the LAPW computations.

NRL-TB and NRL-TBMD

MESP also has a built-in database of Tight-Binding parameter files from one of the NRL websites. If the user does not specify a parameter file for STATIC or TBMD computation, it tries to locate one from its internal database.

Integration

A single interface controls all five programs. Where appropriate, the output from one software is fed as input to the other. The total energy and band energy information is automatically given from the APW or LAPW program to the TBFIT program. MESP understands how to take advantage of symmetry and appropriately manages the input to the TBFIT program.

MESP also creates CDN1 file using APW and feeds it seamlessly to LAPW program to start computation.

History

MESP interfaces with three version control programs: Subversion, CVS, and Mercurial. This enables the user to save all the pertinent files into a repository that can be retrieved later by the same or a different user. It also allows multiple users to work simultaneously on a project. If the users are working on different parts of the project, the version control

software would automatically merge the changes without input. However, if there are merge conflicts, the MESP would require user input before merging files.

When checking-in, the user can put in appropriate comments. These comments are stored along with check-in time and changes made to the project. The user can then retrieve any of the previous versions of project, or visually see differences between files of two different versions.

The user can also create branches from trunk and work from a solidified concept to try a new idea. Later on the user can merge the branch to the trunk or discard the changes that took place in the branch.

Graphical User Interface (GUI)

MESP has a GUI front-end to set up experiments. It is based on Sun's NetBeans Platform. NetBeans is an Integrated Development Environment (IDE). It has many features that are standard to the platform and comes with the same 'look-and-feel' (LNF) of NetBeans.

MESP supports simultaneous editing of multiple files. It provides customized .mesp file editors for all computations. The user can visually select options for a computation.

It also provides a customized viewer for .plot files to view plots. Plots can be superimposed for comparison, zoomed in or out, titles changed, exported as graphic files to be included in documents and can be printed.

Automatic Result Evaluation

The output of running the existing software is evaluated for key elements. The results obtained from one software program may be used as an input to another process or

software. For instance the total energy curve created by APW, LAPW, or STATIC is fed to Birch-Murnaghan fitting process. The fitting process computes the Bulk Modulus that is fed to the process to determine elastic constants, along with the volume computed from the lattice parameter. Without MESP, all these quantities had to be extracted manually from various file outputs and then placed as input for the following program.

Portable Data Format

Whenever possible, MESP uses XML to store information. This includes the .mesp files that stores information regarding the choices a user makes regarding a computation. The .plot files that store data regarding plots is stored in XML. The .plot files can be opened in XML to display interactive plots. Some .properties files are stored in the JAVA .properties format.

Storing in portable formats facilitates sharing data and extending for future re-use.

Getting Started

Installation

MESP is distributed via a zip file. The user may unzip it in a suitable directory. e.g.:

```
cd ~
mkdir ~/.mesp
cd .mesp
unzip mespsuite.zip
```

This would create a `mespsuite` directory.

Invokation

MESP could be invoked by something like:

~/.mesp/mespsuite/bin/mespsuite

Upon running for the first time, MESP creates a hidden directory in the user's home directory (`~/.mesp`) to store temporary files, history information, logs, input and output files to the underlying software.

Getting Familiar with NetBeans

The NetBeans Integrated Development Environment (IDE) has various sub-windows that display respective information. These sub-windows are displayed in the areas shown below.

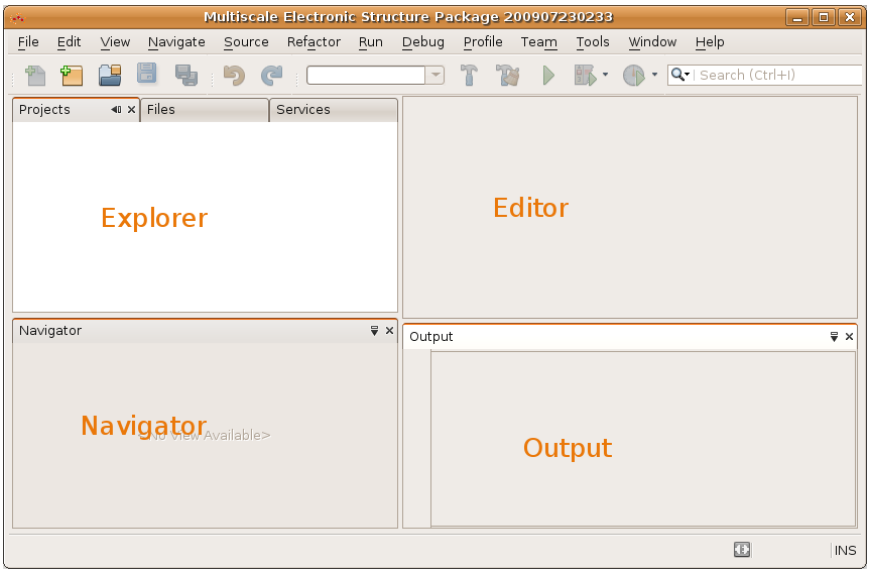

Figure 2: A view of the application, showing various areas for windows.

Each of these sub-windows can be closed and then opened again. If a particular window is not visible, simply click on the **Window** menu option on the main menu bar and select the desired window.

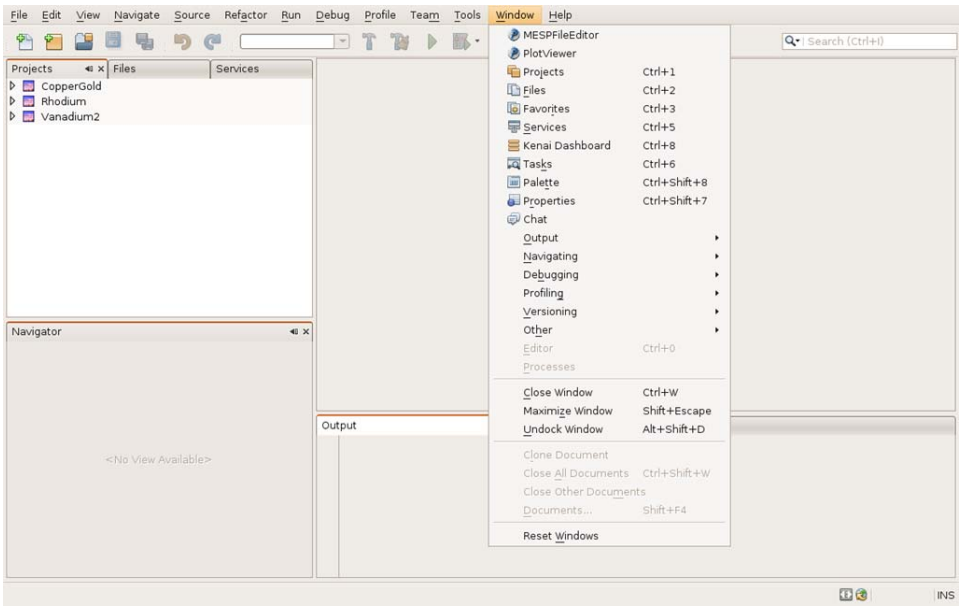

Figure 3: Opening a closed sub-window.

For detailed information about NetBeans, please visit netbeans.org.

Using a Sample Project

Once MESP has started, click on **File | New Project ...** to start the new project wizard.

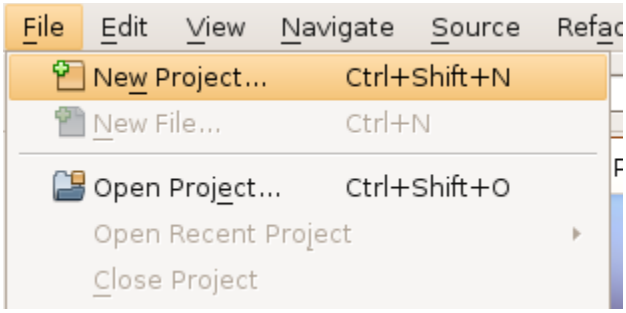

Figure 4: Starting the New Project Wizard

It contains two selection boxes. The left selection box is titled **Categories**. Select **Multi-purpose Electronic Structure Package**. The right selection box would display available projects.

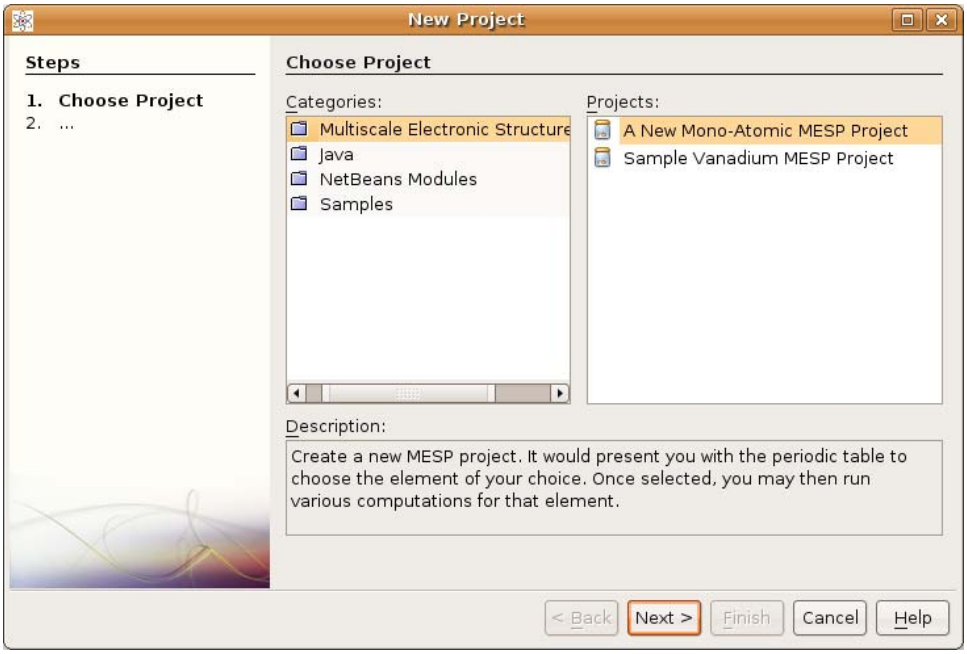

Figure 5: First screen of New Project Wizard.

Select **Sample Vanadium MESP Project** and click on the **Next** button. This would present you with a screen asking for Project Name. Enter a name for the project, or leave it with whatever is entered already. As you change the Project Name, other fields may also get modified.

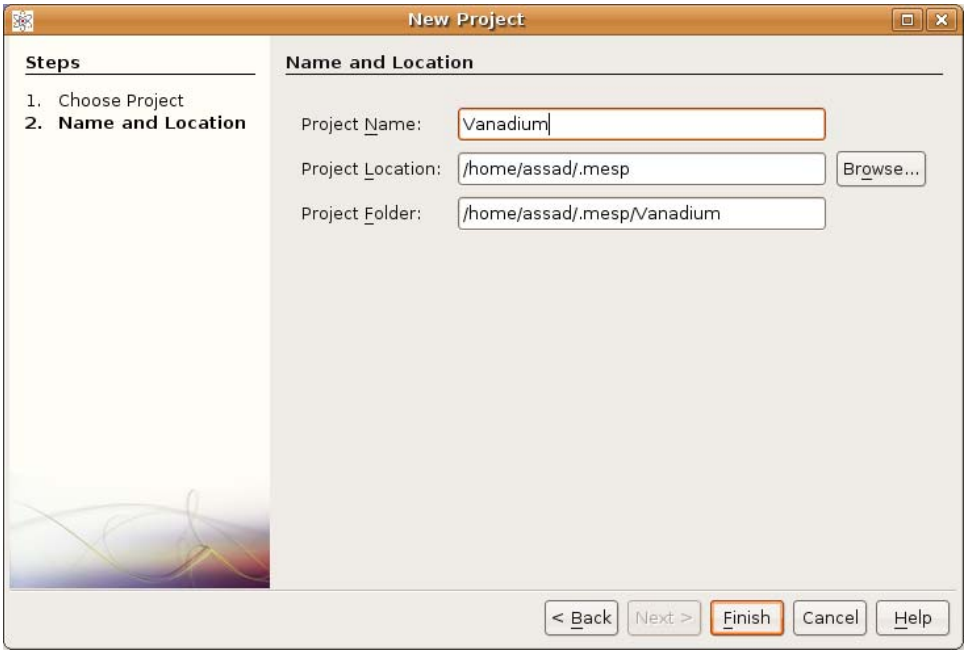

Figure 6: Second screen of the New Project Wizard.

Clicking on **Finish** button would create the project in your **Project** window.

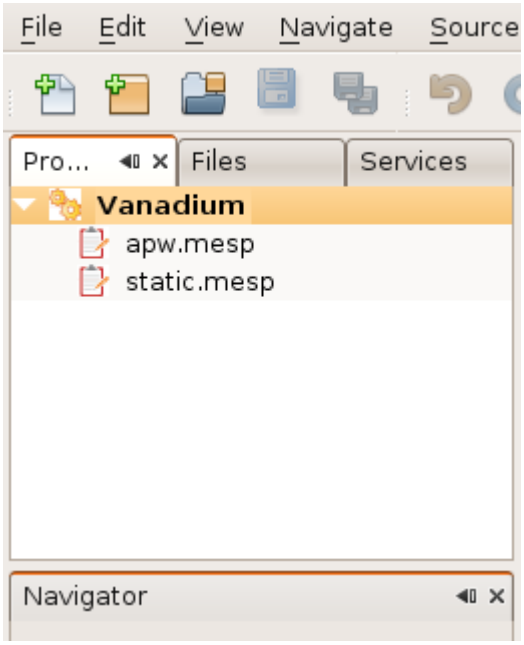

Figure 7: Newly created project shown in the Explorer area of the application.

Creating a New Project

To create a new project, click on **File | New Project ...** and MESP would present a facility to create new projects.

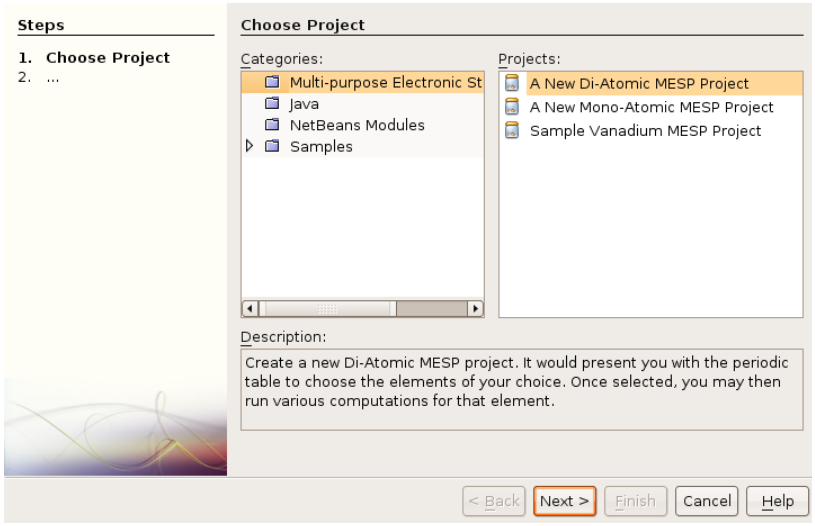

Figure 8: Creating a new project.

Select **Multi-purpose Electronic Structure Package** in the left list box and either **A Mono-Atomic MESP Project** or **A diatomic MESP Project** in the right list box.

Clicking on **Next** would yield a screen to select either one or two elements.

Figure 9: Selecting an element for the project.

Clicking on the **Next** button would present a screen to select a name and a directory for this project.

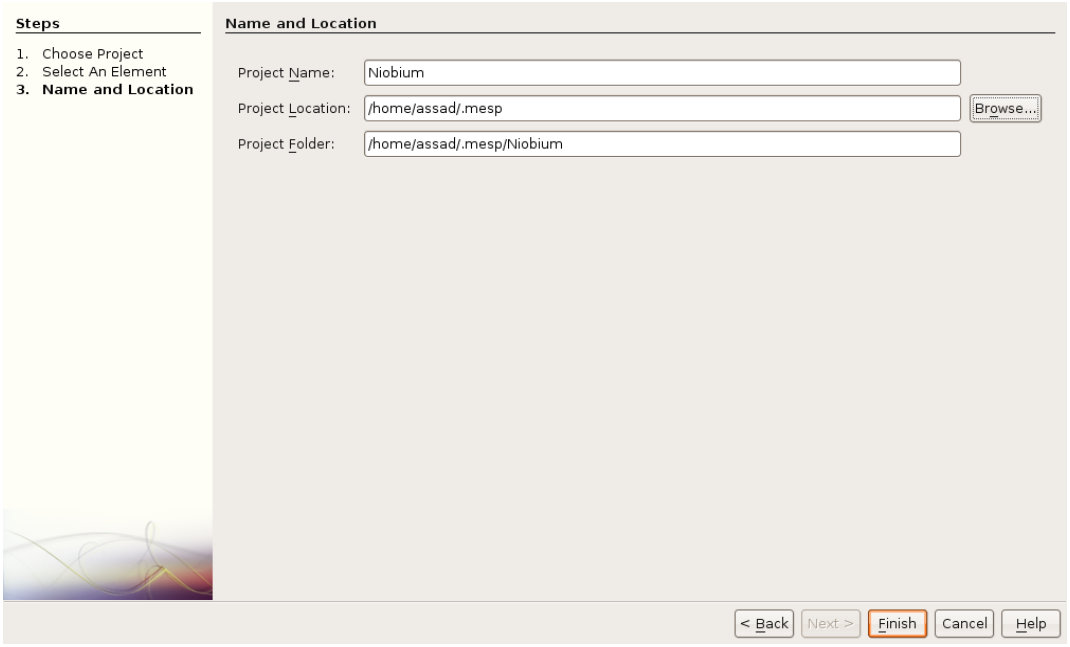

Figure 10: Selecting a name and a project directory for the newly created project.

Upon clicking **Finish**, MESP would create the directory indicated in **Project Folder** input field and the following three directories in it:

```
computations
configurations
mespproject
```

MESP Lattice Parameter Estimation

Out of the box, total energy computations using APW, LAPW, and STATIC require the user to provide an approximate equilibrium lattice parameter. MESP estimates this lattice parameter from its database of experimental lattice parameters. In case there is no

experimental lattice parameter for the selected crystalline structure, MESP estimates it by equating the volume per atom of the crystalline structure for which the lattice parameter is known with the volume of the crystalline structure for which the lattice parameter is not known. Thus if the lattice parameter of a particular material is known is BCC crystalline structure, the lattice parameter for the FCC crystalline structure can be estimated as follows:

$$a_{FCC} = a_{BCC} 2^{1/3} \tag{17}$$

The estimated lattice parameter is rounded off to the nearest tenth of a bohr and a range of +/- 0.5 bohr around that estimated point is evaluated.

MESP Interactive Plotting Facility

Several of the MESP computations produce a **plots** directory. This directory contains some plots that can be managed interactively. Right click on one of the plots and click on the **Plot** menu option from the pop-up menu to open the file as a plot in the **Editor** area.

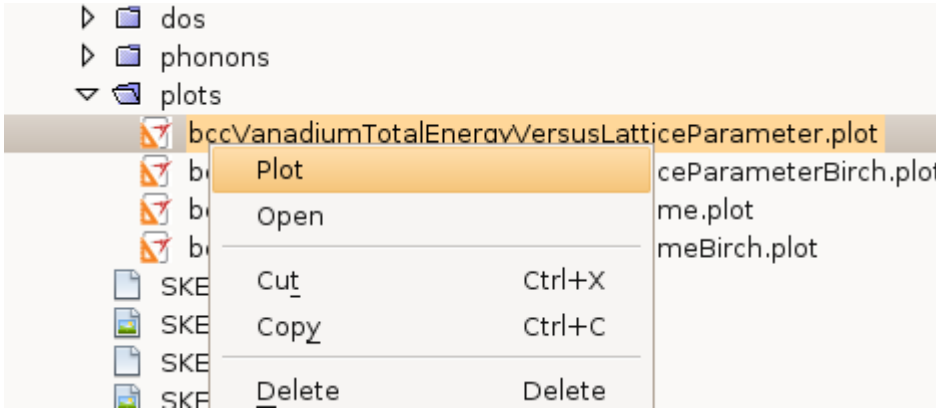

Figure 11: Click on the 'Plot' option to plot the curve.

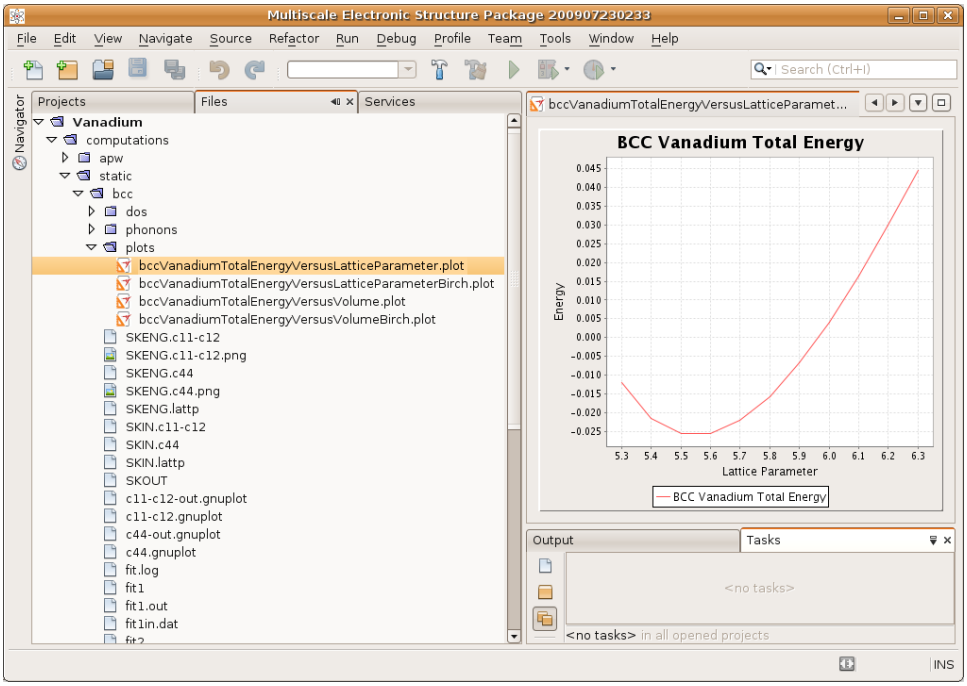

Figure 12: A total energy curve being displayed in the 'Editor' area.

One can also double-click to file to get the same result.

Additionally, one can right click on it and then click on the **Open** option to view or edit the underlying XML data.

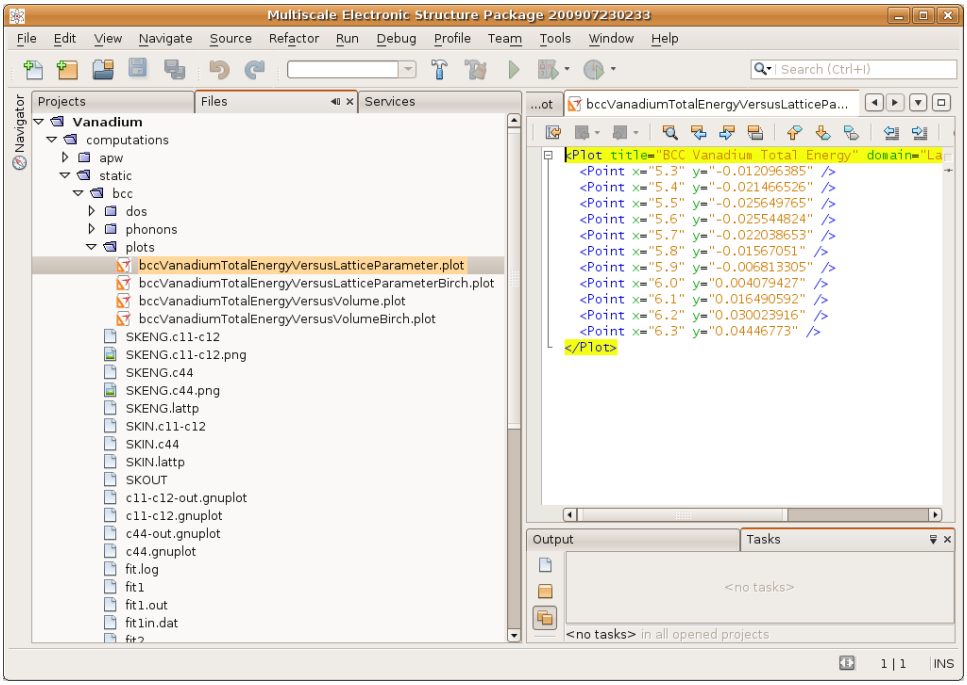

Figure 13: Editing XML data of the plot file.

Dragging a plot file onto another open plot file in the plotting mode (and not XML mode) overlays that plot over the existing plot. The example below shows the computed total energy plot along with the Birch Fit total energy plot. It was obtained by dragging the Birch Fit plot onto the already open plot of total energy versus lattice parameter.

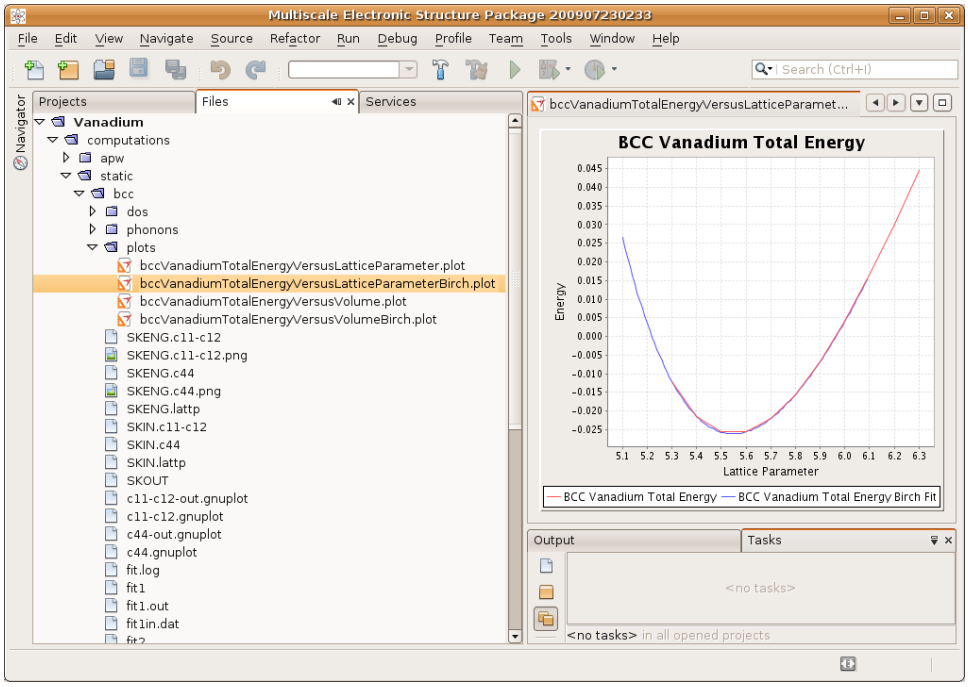

Figure 14: Two plot files displayed together in a plot.

The legend for the combined plot is automatically updated.

Selecting a region on the displayed plot zooms in.

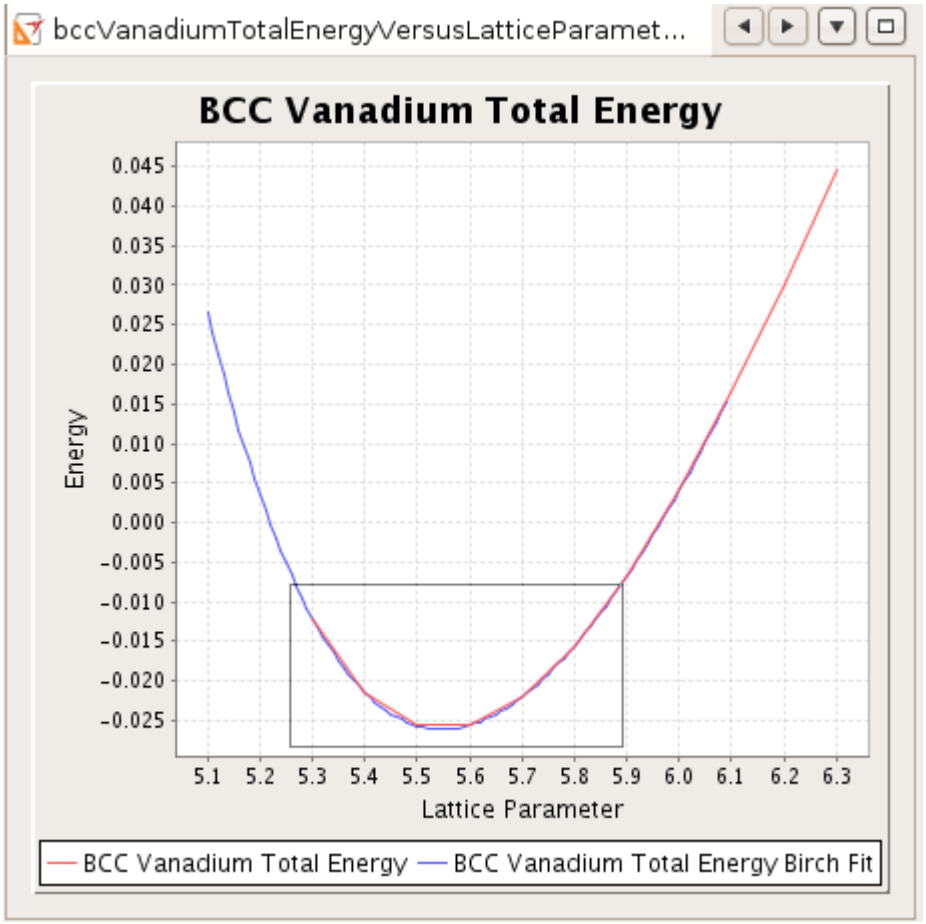

Figure 15: Selecting a region zooms in.

Hovering the mouse over a point in the plot would display the data values.

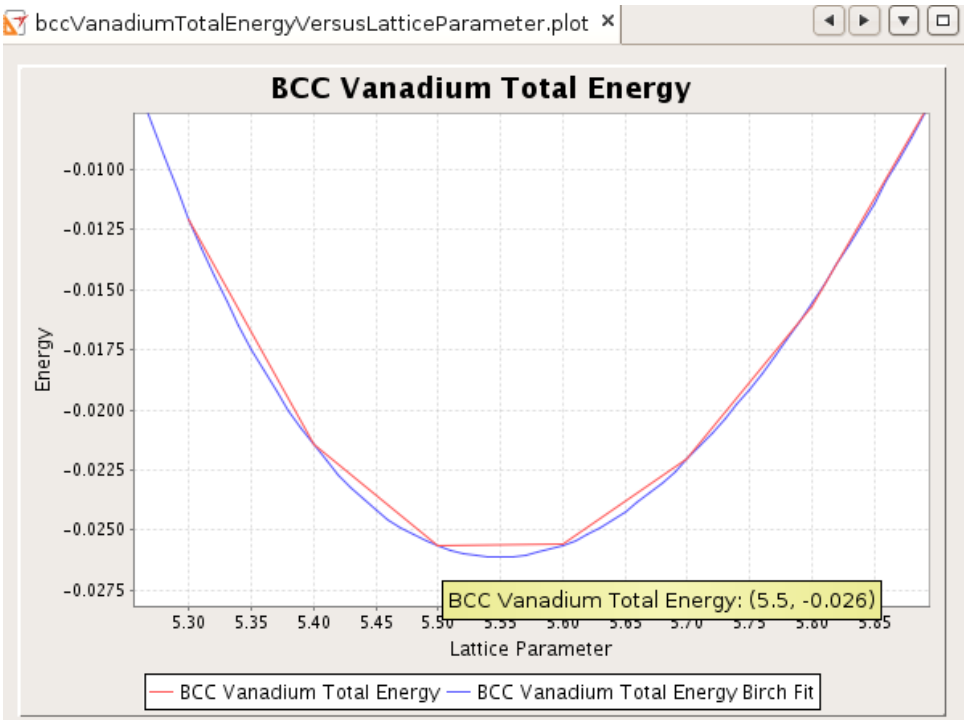

Figure 16: Hovering mouse over a point displays data values.

Right click anywhere in the plotting region to display menu to work with the plot.

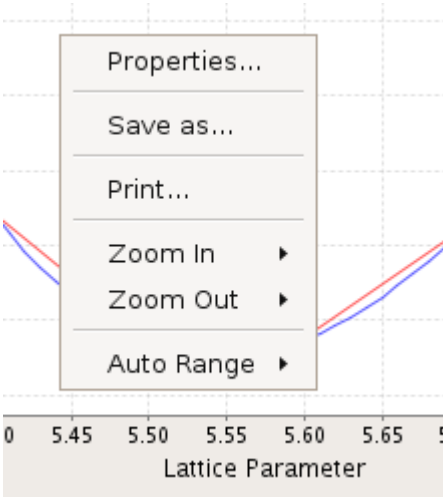

Figure 17: Plotting pop-up menu.

Select **Properties** to change plot and axes titles, among other plot related options

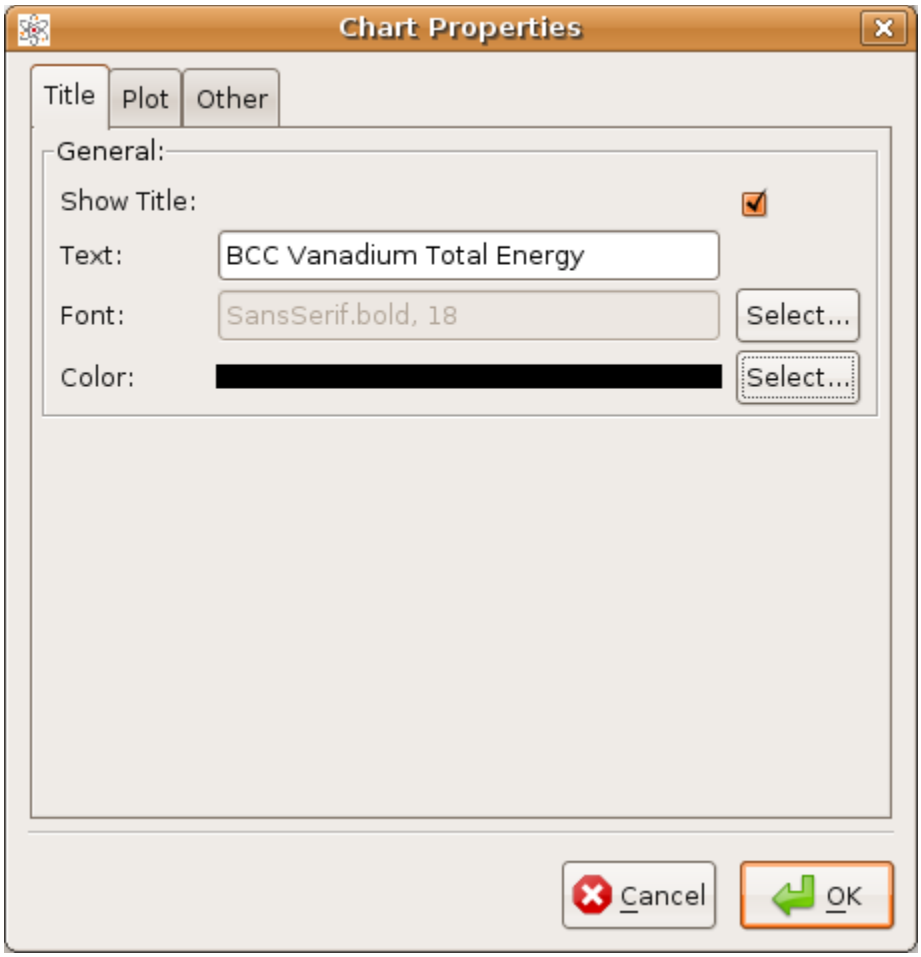

Figure 18: Plot Properties window

To zoom out to the default level, right click on the plotting area, select **Auto Range | Both Axes**.

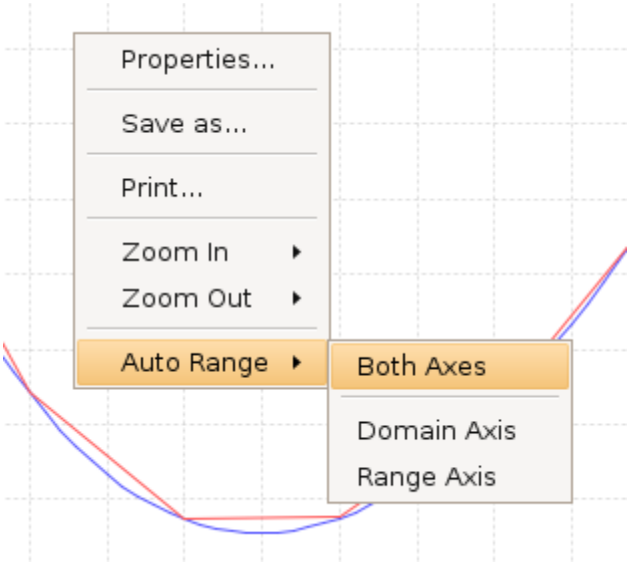

Figure 19: Resetting zoom to default.

To print, right click on the plotting area and select **Print ...**. To save the plot as an image file, right click on the plotting area and select **Save as ...**. This would present a file dialog to save as a PNG image.

Using the information about plotting presented above, one can now open a BCC total energy versus volume plot and then go to the **FCC** directory to get a similar plot of total energy versus volume and drag it to the already open plot. Changing the plot title by right clicking on the plot and selecting **Properties** would display a plot similar to the following.

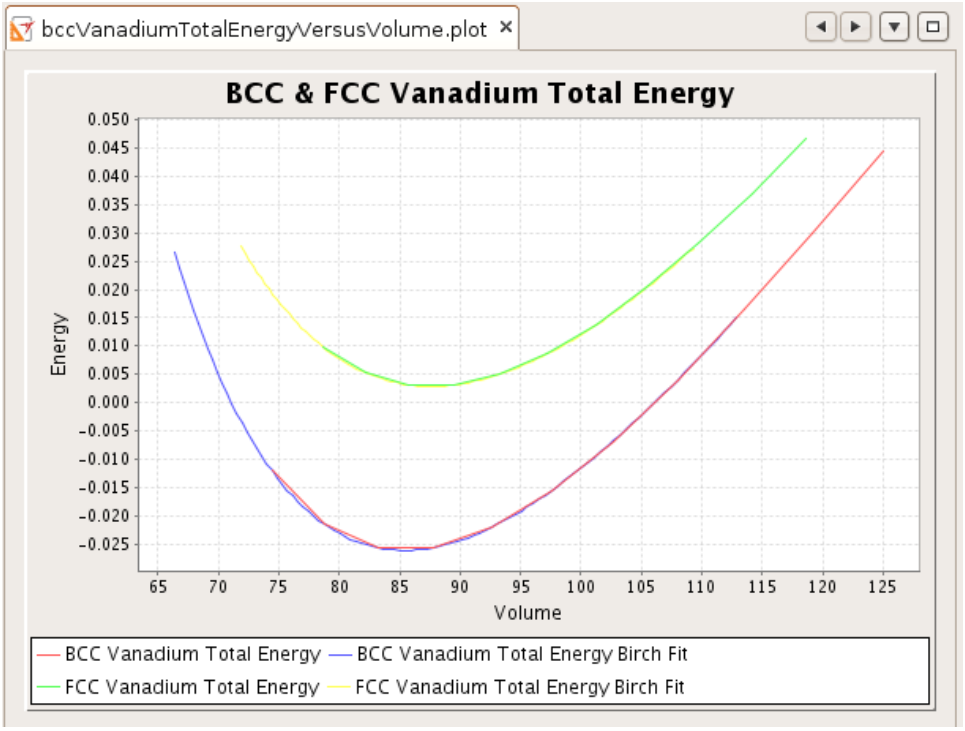

Figure 20: A combined plot of BCC and FCC total energy versus volume.

Right-clicking and selecting **Open**, or double-clicking on any PNG, JPEG, or GIF file opens the image in the **Editor** area.

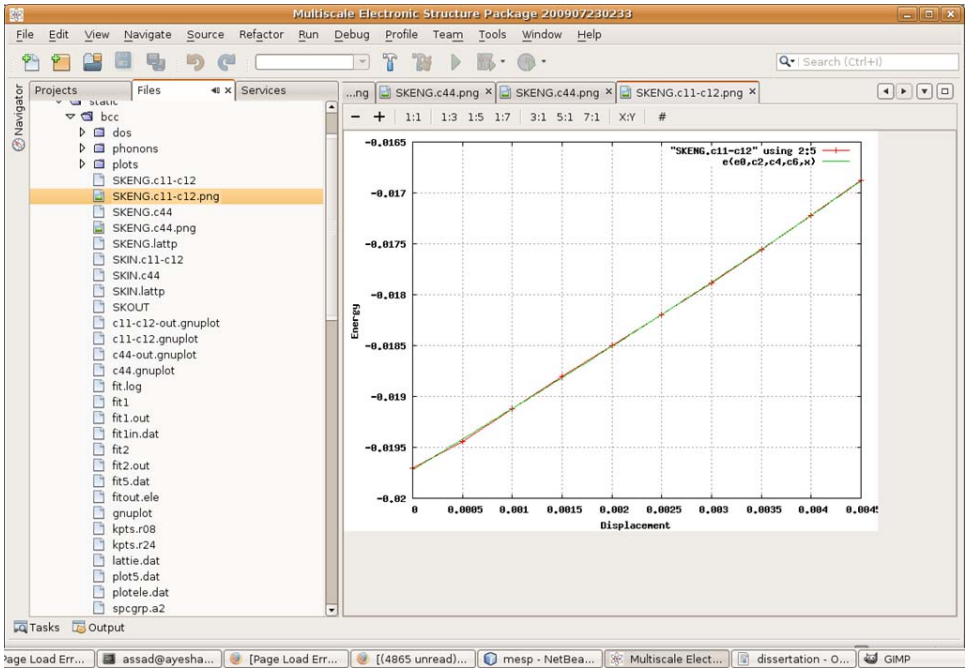

Figure 21: Displaying a .png file in 'Editor' area.

The sample plot above comes from using STATIC to compute elastic constants.

Chapter 4: APW With MESP

This chapter is more specific to APW calculations including the calculation of energy bands and densities of states.

Supported Crystalline Structures for APW Computations

MESP supports the following mono-atomic crystalline structures for APW computations:

- Simple Cubic (SC)
- Body Centered Cubic (BCC)
- Face Centered Cubic (FCC)
- It also supports the following diatomic crystalline structures:
- Sodium Chloride (NaCl)
- Cesium Chloride (CsCl)

Input for APW Computations

By clicking on the .mesp file of APW, MESP provides in the **Editor** section a facility to enter the following quantities for APW computations:

- Estimated lattice parameter for each of the crystalline structures mentioned above
- The range around the estimated lattice parameter to compute total energy

- A selection of six or nine energy bands. If this APW computation results are to be fed to NRL-TBFIT, the user must select six energy bands, in case of transition metals.
- Minimum and Maximum energy window to perform computations. A reliable choice of energy window for transition metals is -0.5 to 2.0 Rydbergs.

Once these options are selected, the user must then save the .mesp file for the changes to take effect. Please note that the units used are bohr for length and Rydberg for energy.

Running APW

Right click on the apw.mesp file in the project and click on **Compute**.

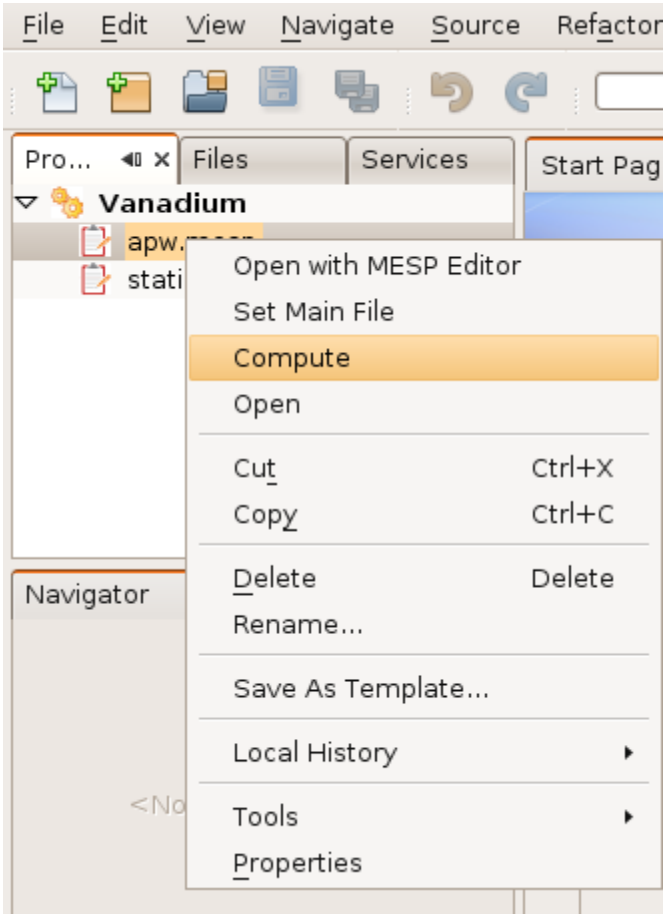

Figure 22: Click on the 'Compute' option of the pop-up menu.

This would run APW with default options. You should notice APW output in the Output area.

If you want to modify the APW options, right click on apw.mesp and click on **Open with MESP Editor**. This would open an editor in the **Editor** area.

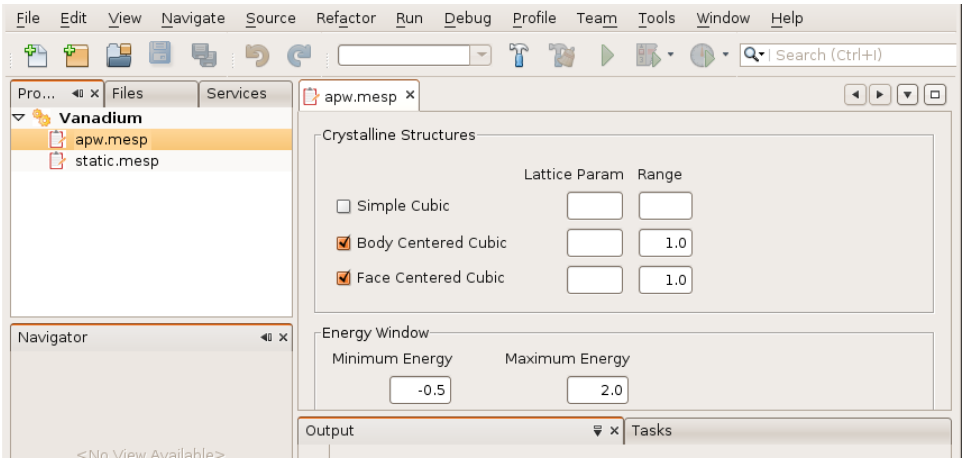

Figure 23: Editing apw.mesp file with MESP editor.

You may change APW options and the click on **File | Save** to save changes. To run APW again, right click on **apw.mesp** file and click on **Compute**.

Inspecting APW Results

Click on the **Files** tab in the **Explorer** area of the application. It would show you the projects that you have opened. Open the one that is being currently working on. Three directories labeled **computations**, **configurations**, and **mespproject**. Open the **computations** directory to reveal the programs that you have run in this project. Open the **apw** directory, showing the crystalline structures used in the computation. These directories would contain the results of the computations.

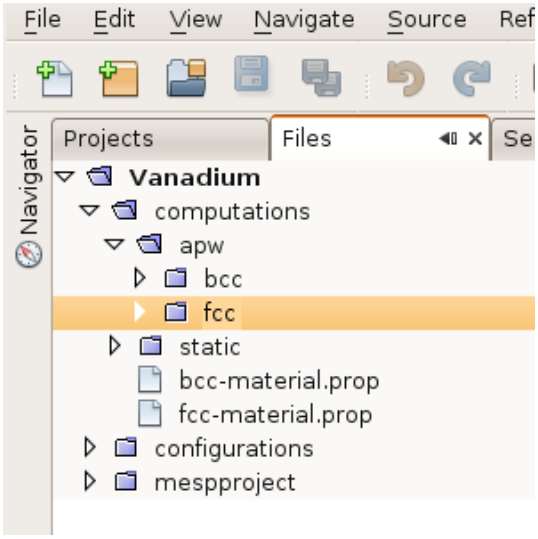

Figure 24: Computations results directory structures.

Click on one of the crystalline structures. The application would display the computational results of APW for total energy, energy bands, and density of state calculations. One may double-click on a PNG file to open it in the **Editor** area. The same result may also be achieved by right clicking on a PNG file and then selecting **Open** menu option.

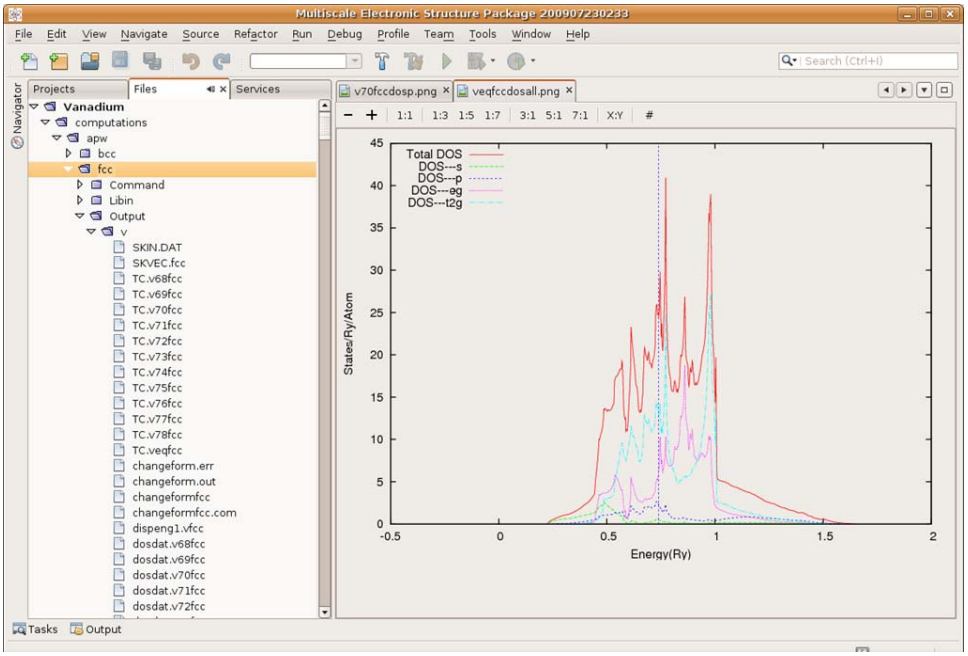

Figure 25: APW calculation results

Sample Computations with Copper

Using MESP to execute APW produced the following plot of volume vs. total energy for the FCC and BCC computations.

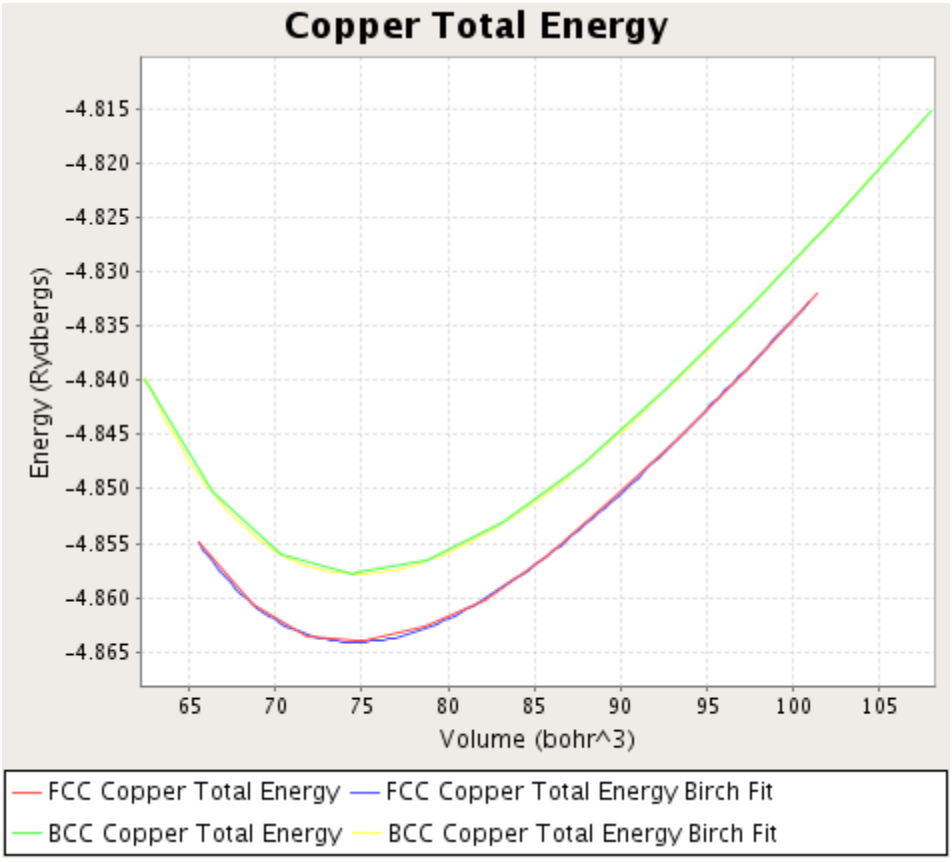

Figure 26: Volume vs. Total Energy for FCC and BCC structures of Copper

This plot shows that Copper prefers FCC structure in ground state as the FCC curve is lower in energy compared to the BCC curve.

The following table summarizes the results of the computations.

Table 1 Lattice Parameters and Bulk Moduli of Copper computed via APW

Structure	*Lattice Parameter (bohr)*	*Bulk Modulus (GPA)*
BCC	5.31	181.38
FCC	6.68	188.32

For FCC structure at equilibrium parameter the following energy bands and density of states were computed.

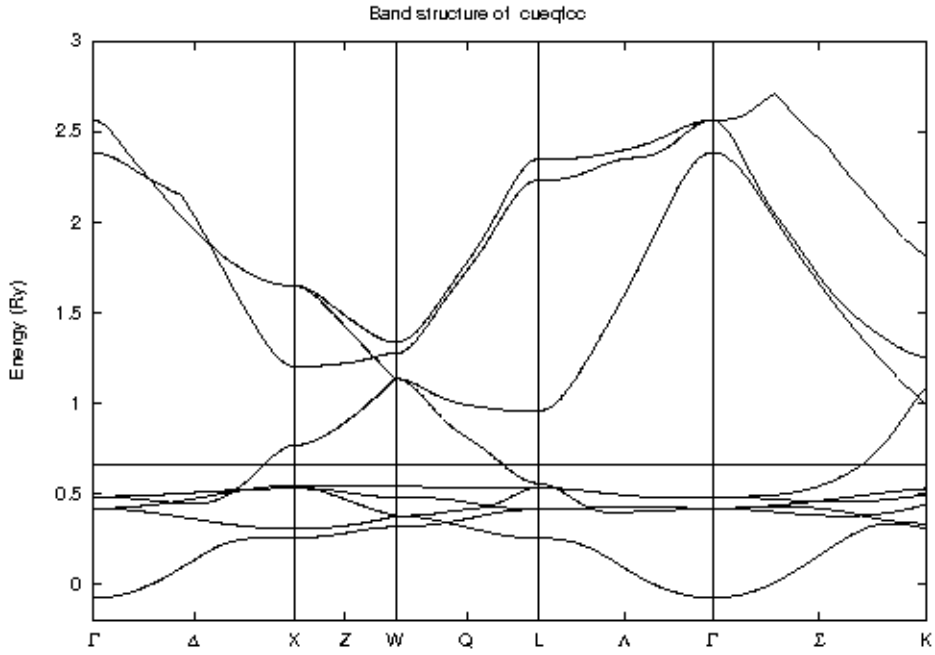

Figure 27: Energy bands of Copper at equilibrium parameter of FCC structure.

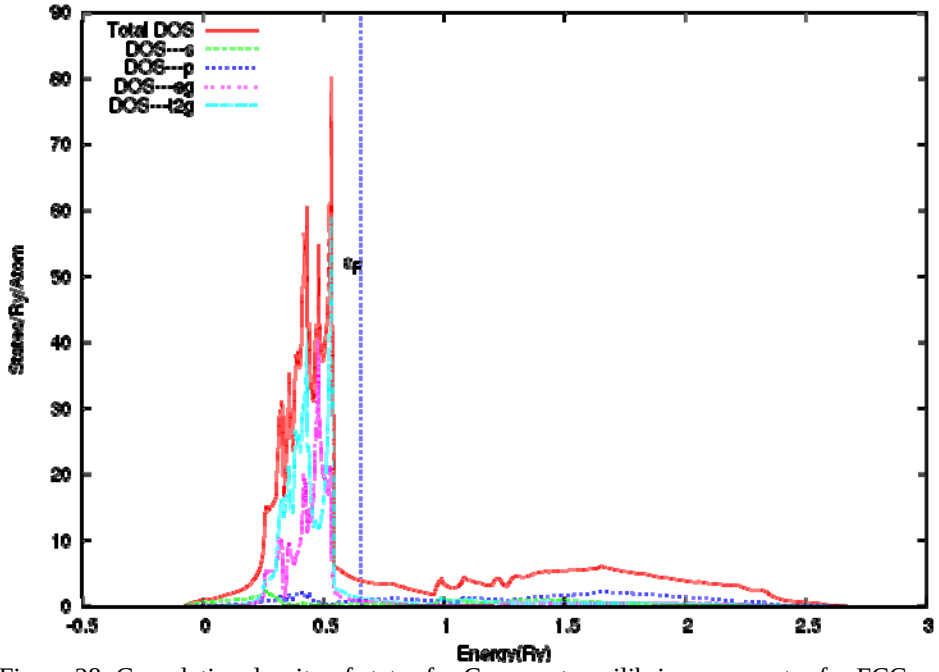

Figure 28: Cumulative density of states for Copper at equilibrium parameter for FCC structure.

Sample Computations with Vanadium

Using MESP to execute APW produced the following plot of volume vs. total energy for the FCC and BCC computations.

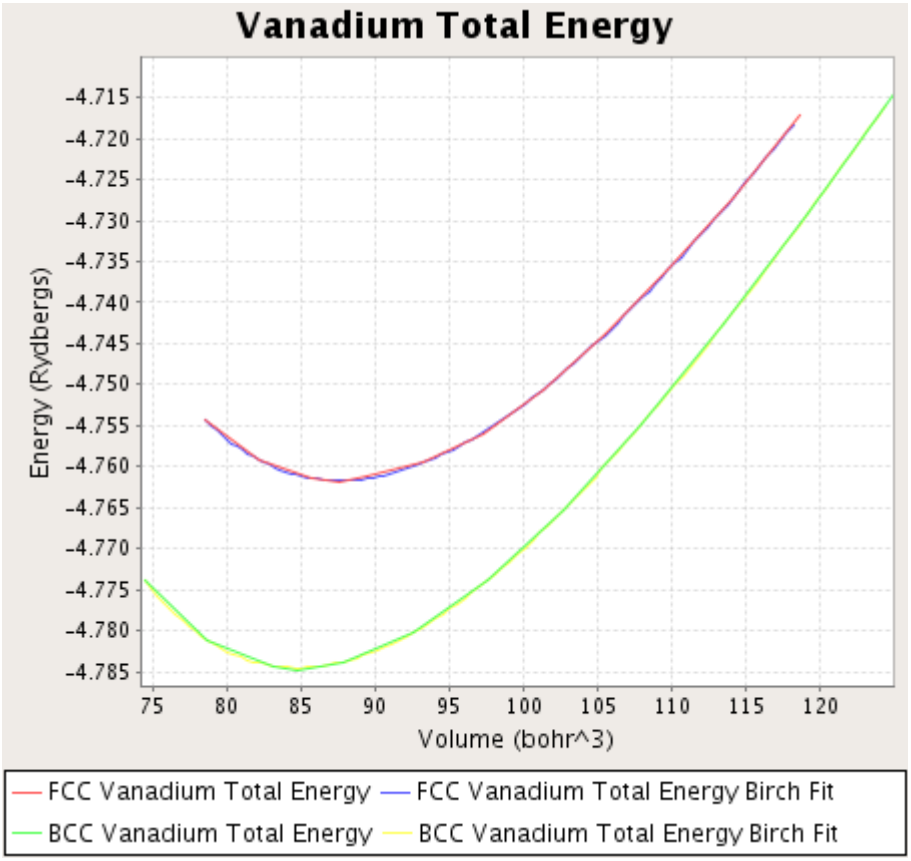

Figure 29: Total Energy vs. Volume for FCC and BCC structures of Vanadium

This plot shows that Vanadium prefers BCC structure in ground state as the BCC curve is lower in energy compared to the FCC curve.

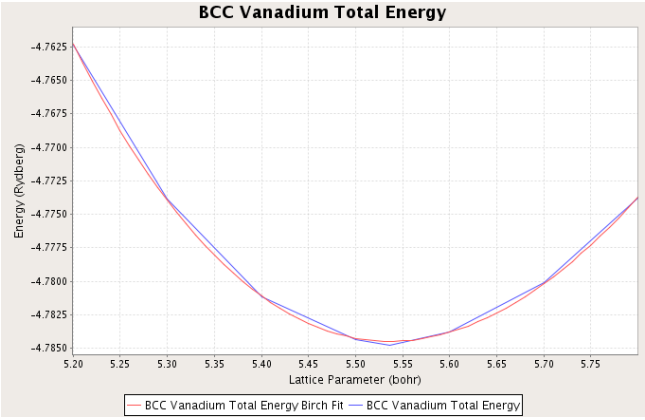

Figure 30: Total Energy as a function of lattice parameter for Vanadium in BCC structure as computed by APW program.

The following table summarizes the results of the computations.

Table 2 Lattice Parameters and Bulk Moduli of Vanadium computed via APW

Structure	*Lattice Parameter (bohr)*	*Bulk Modulus (GPA)*
BCC	5.53	202.71
FCC	7.05	193.31

The band energies for BCC Vanadium at equilibrium lattice parameter were computed as:

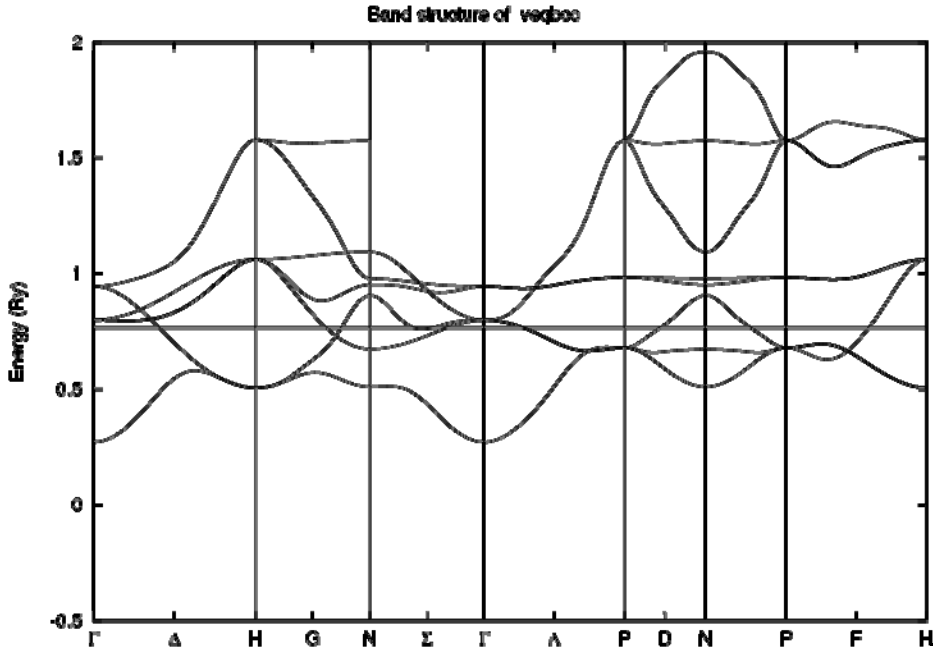

Figure 31: Band energies for BCC Vanadium at equilibrium lattice parameter.

And the density of states also for BCC Vanadium at equilibrium lattice parameter are shown below:

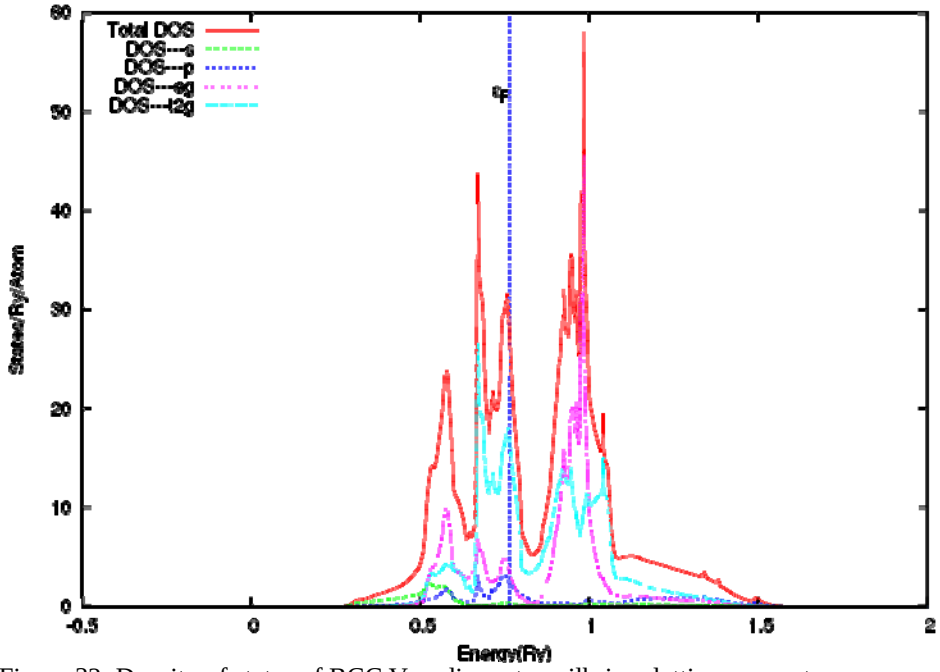

Figure 32: Density of states of BCC Vanadium at equilbrium lattice parameter.

Since the fermi energy passes through the bands and the density of states plots, Vanadium is a conductor in ground state.

Sample Computations with Titanium-Nickel (TiNi)

Sodium Chloride (NaCl) Crystalline Structure

Using MESP to execute APW produced the following plot of lattice parameter vs. total energy for the NaCl computations.

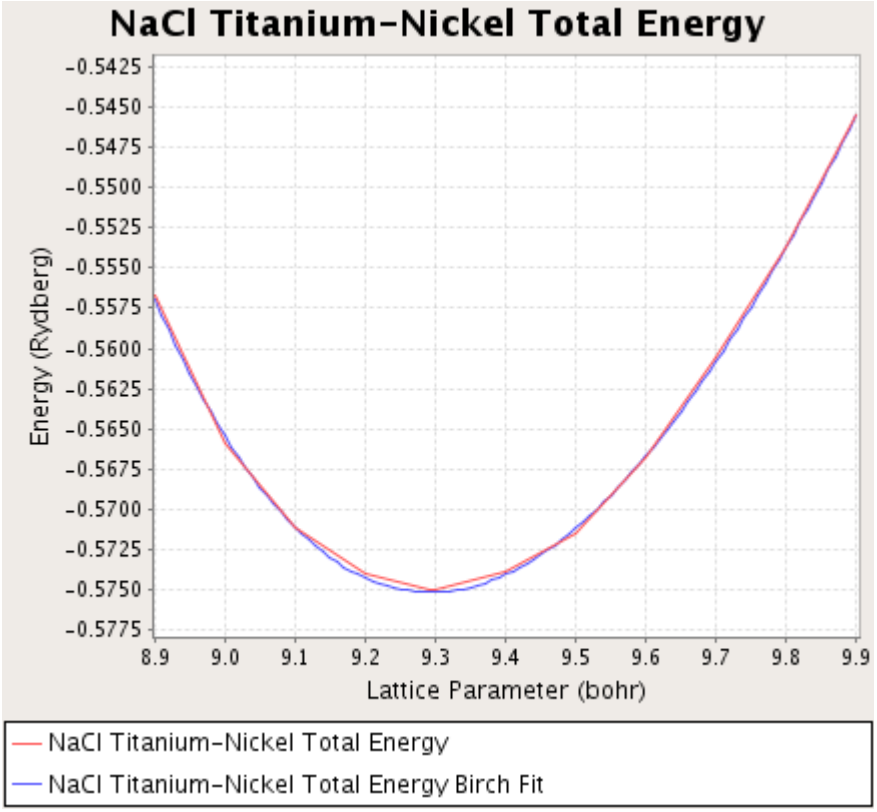

Figure 33: Total Energy vs. Lattice Parameter of Titanium-Nickel (TiNi) in Sodium-Chloride (NaCl) crystalline structure.

Additionally, the band structure computed for the NaCl crystalline structure is presented below:

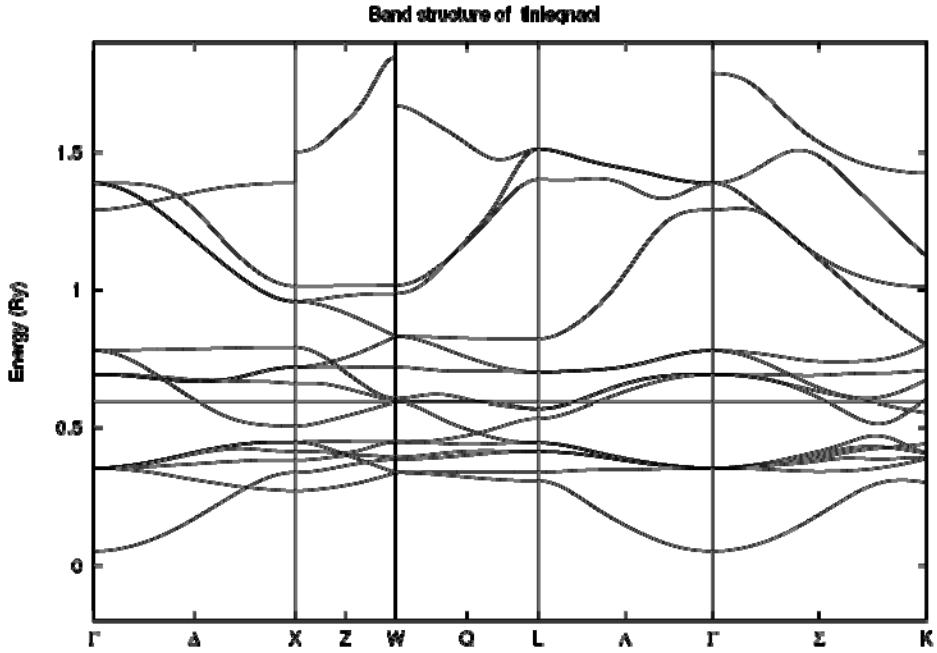

Figure 34: The band structure of NaCl crystalline structure Titanium-Nickel (TiNi) at equilibrium lattice parameter.

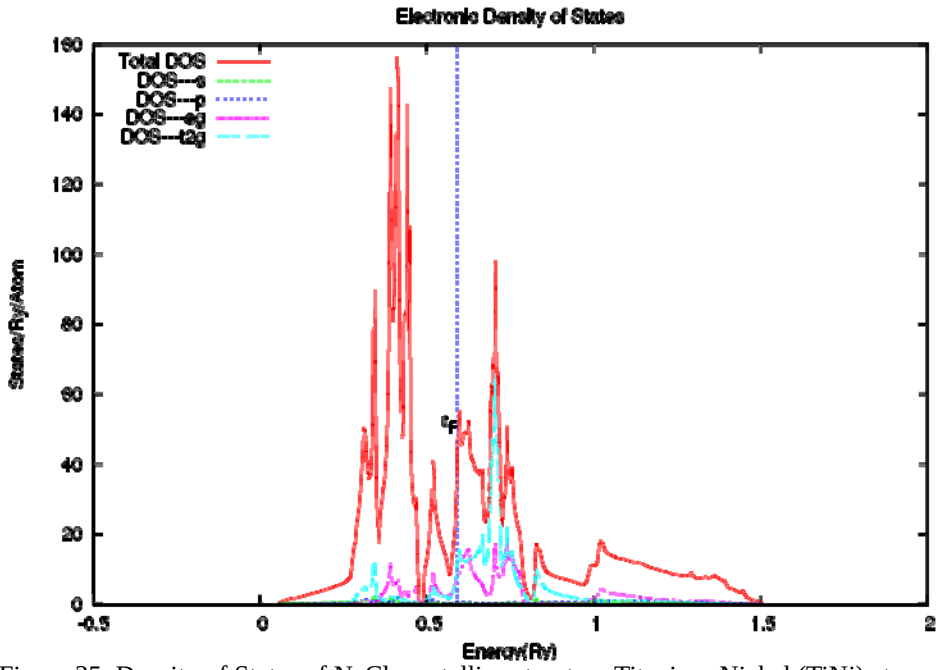

Figure 35: Density of States of NaCl crystalline structure Titanium-Nickel (TiNi) at equilibrium parameter.

The density of states computed for CsCl structure is depicted below:

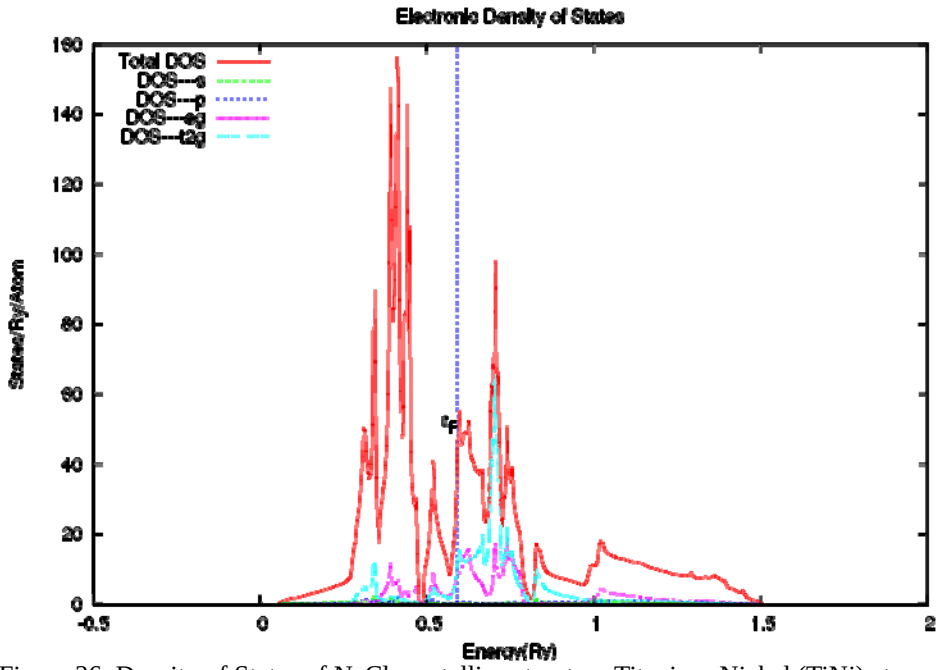

Figure 36: Density of States of NaCl crystalline structure Titanium-Nickel (TiNi) at equilibrium parameter.

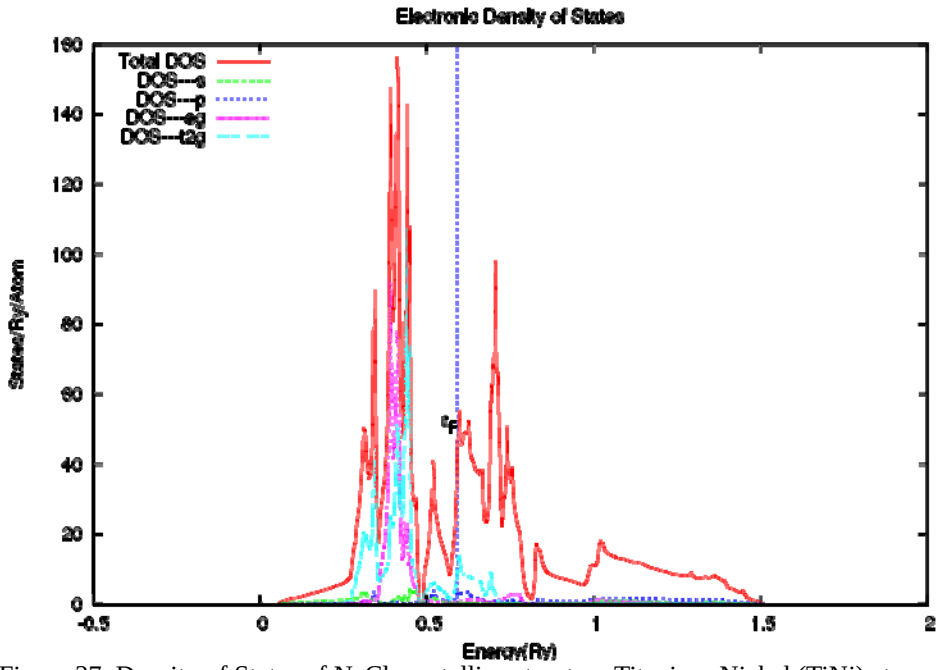

Figure 37: Density of States of NaCl crystalline structure Titanium-Nickel (TiNi) at equilibrium parameter.

Cesium Chloride (CsCl) Crystalline Structure

Using MESP to execute APW produced the following plot of lattice parameter vs. total energy for the CsCl computations.

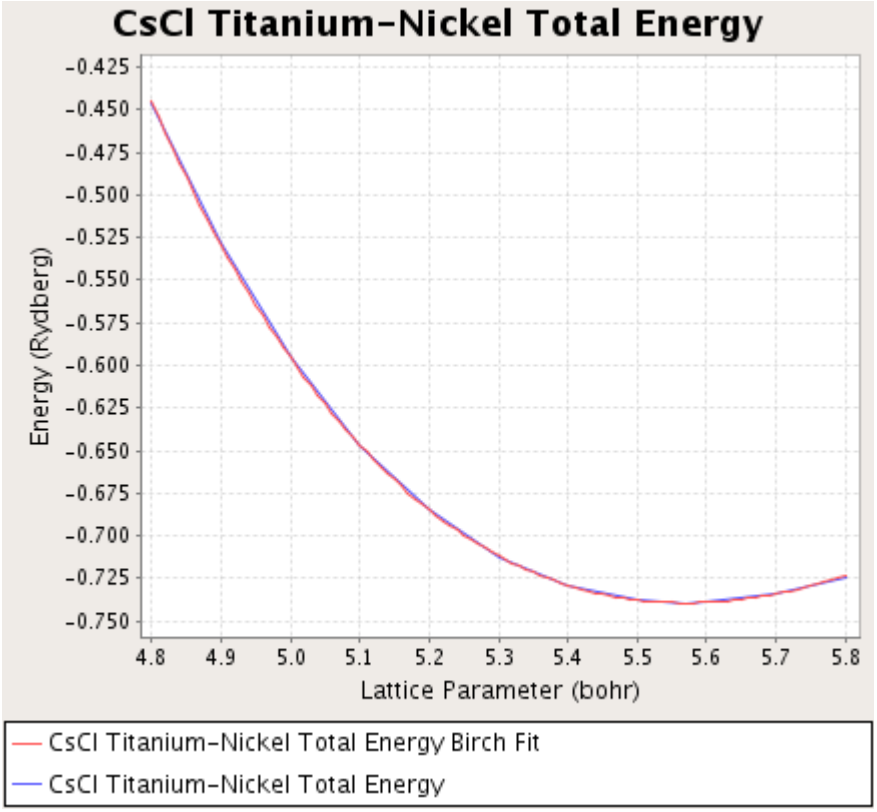

Figure 38: Total Energy vs. Lattice Parameter of Cesium Chlordie (CsCl) crystalline structure of Titanium-Nickel (TiNi).

Additionally, the band structure computed for the CsCl crystalline structure is presented below:

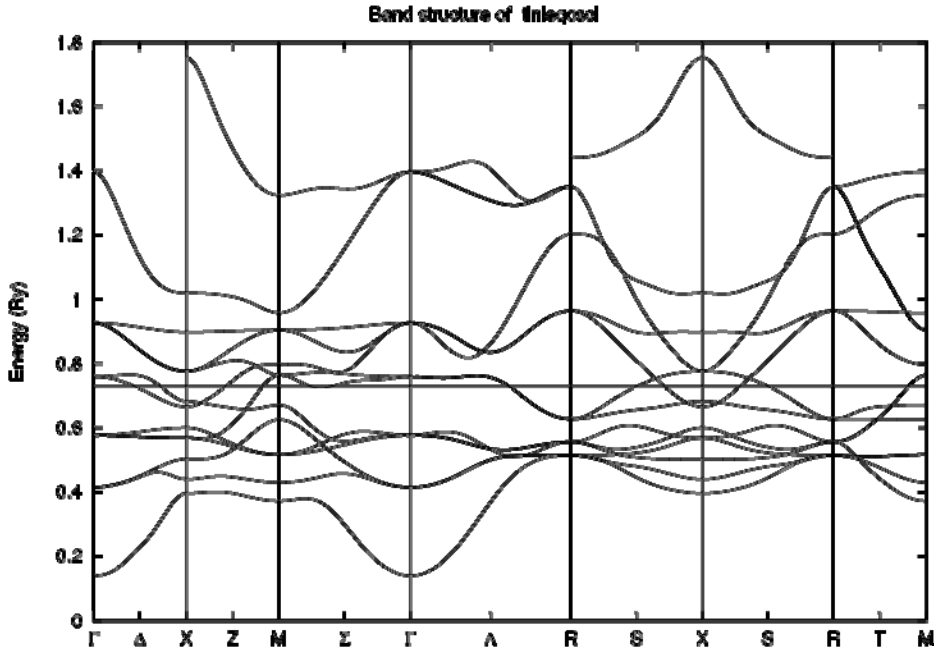

Figure 39: Band Structure of Cesium-Chloride (CsCl) crystalline structure Titanium-Chloride (TiNi) at equilibrium lattice parameter. The horizontal line shows the fermi level.

The density of states computed for CsCl structure is depicted below:

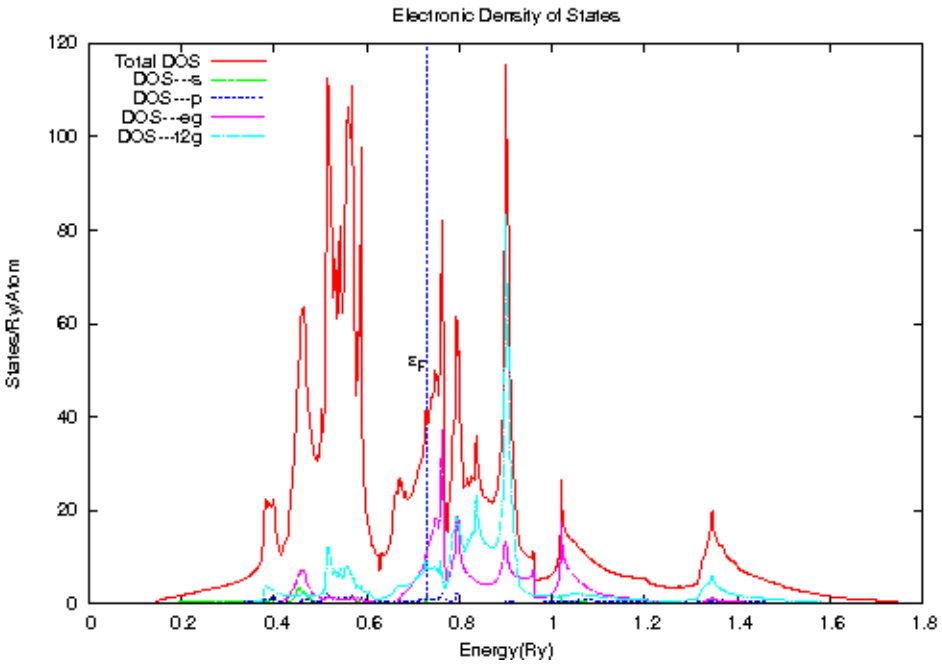

Figure 40: Density of States (DOS) of Cesium-Chloride (CsCl) crystalline structure Titanium-Chloride (TiNi) at equilibrium lattice parameter.

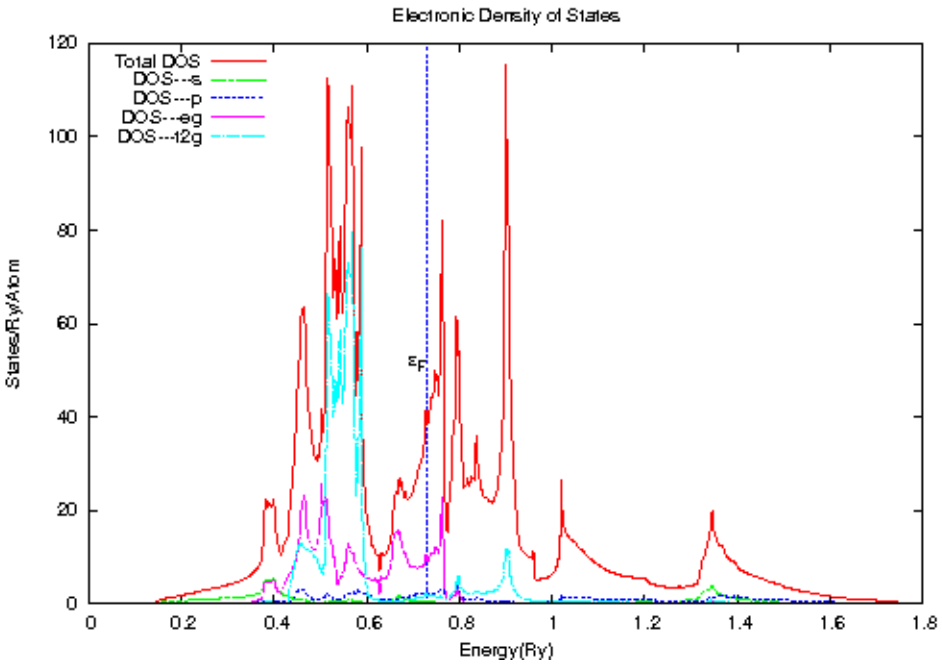

Figure 41: Density of States of Cesium-Chloride (CsCl) crystalline structure Titanium-Chloride (TiNi) at equilibrium lattice parameter. The vertical line shows the fermi level.

Ground State Crystalline Structure

The following plot shows total energy as a function of volume. The lower energy CsCl equilibrium lattice parameter indicates that TiNi prefers CsCl structure at ground state.

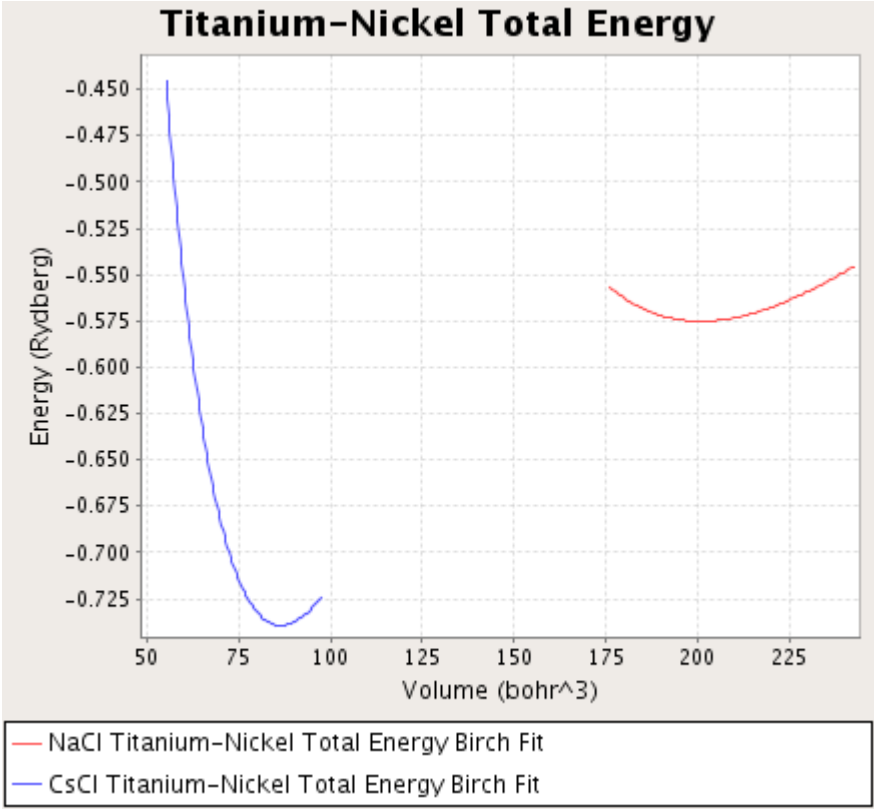

Figure 42: Comparison of total energy vs. volume of NaCl and CsCl structures.

The following table summarizes the results of the computations.

Table 3 Lattice Parameters and Bulk Moduli of TiNi computed via APW.

Structure	*Lattice Parameter (bohr)*	*Bulk Modulus (GPA)*
NaCl	9.29	141.97
CsCl	5.57	192.71

Chapter 5: LAPW With MESP

Supported Crystalline Structures for LAPW Computations

MESP supports the following crystalline structures for LAPW computations:

- Simple Cubic (SC)
- Body Centered Cubic (BCC)
- Face Centered Cubic (FCC)

Input for LAPW Computations

By clicking on the .mesp file of LAPW, MESP provides in the **Editor** section a facility to enter the following quantities for LAPW computations:

- Estimated lattice parameter for each of the crystalline structures mentioned above
- The range around the estimated lattice parameter to compute total energy
- A selection of six or nine energy bands. If this LAPW computation results are to be fed to NRL-TBFIT, the user must select six energy bands.
- Minimum and Maximum energy window to perform computations
- Initial charge density file (CDN1)

Once these options are selected, the user must then save the .mesp file for the changes to take effect.

Running LAPW

Right click on the lapw.mesp file in the project and click on **Compute**.

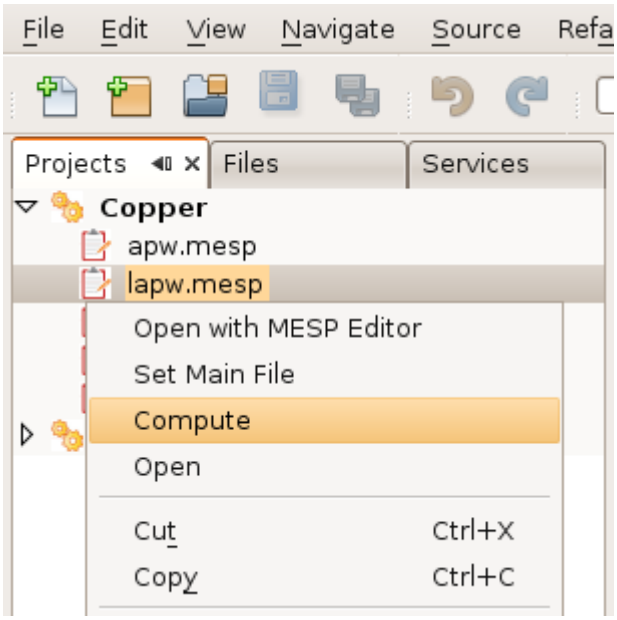

Figure 43: Click on the 'Compute' option of the pop-up menu.

This would run LAPW with default options. You should notice LAPW output in the Output area.

If you want to modify the LAPW options, right click on lapw.mesp and click on **Open with MESP Editor**. This would open an editor in the **Editor** area.

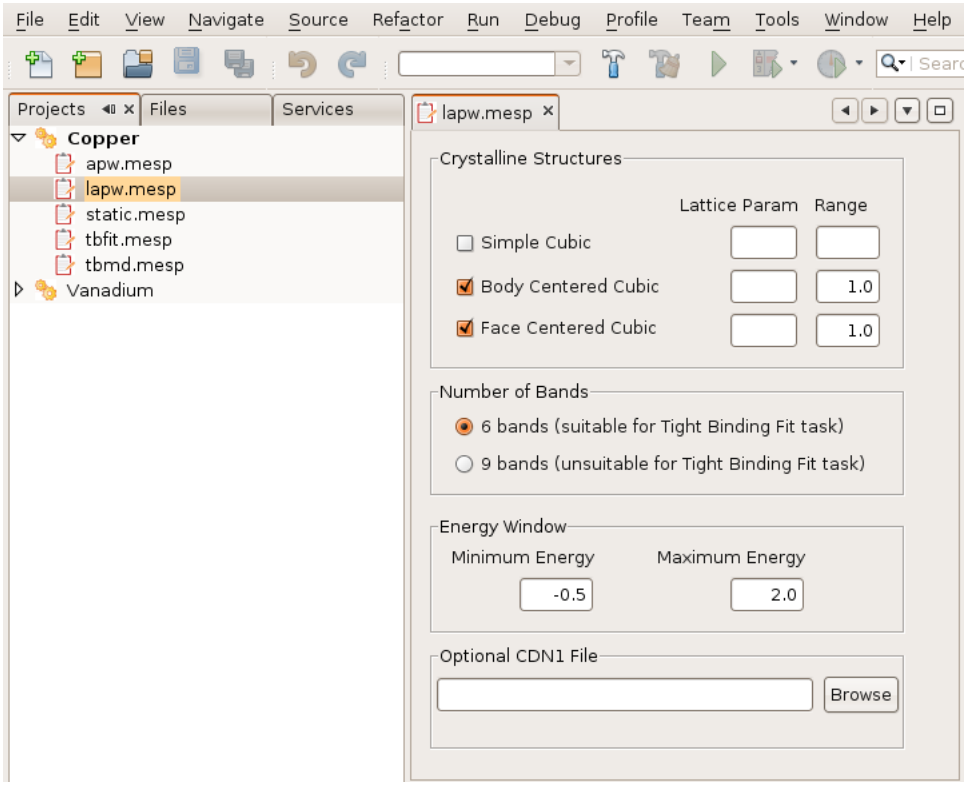

Figure 44: Editing lapw.mesp file with MESP editor.

You may change LAPW options and the click on **File | Save** to save changes. If you leave out the lattice parameters, MESP would try to make an educated guess depending upon experimental values. If you leave out the CDN1 file, it would run a small APW run in order to generate initial CDN1 file. To run LAPW again, right click on apw.mesp file and click on **Compute**.

Inspecting LAPW Results

Click on the **Files** tab in the **Explorer** area of the application. It would show you the projects that you have opened. Open the one that is being currently working on. Three directories labeled **computations**, **configurations**, and **mespproject**. Open the **computations** directory to reveal the programs that you have run in this project. Open the **lapw** directory, showing the crystalline structures used in the computation. These directories would contain the results of the computations.

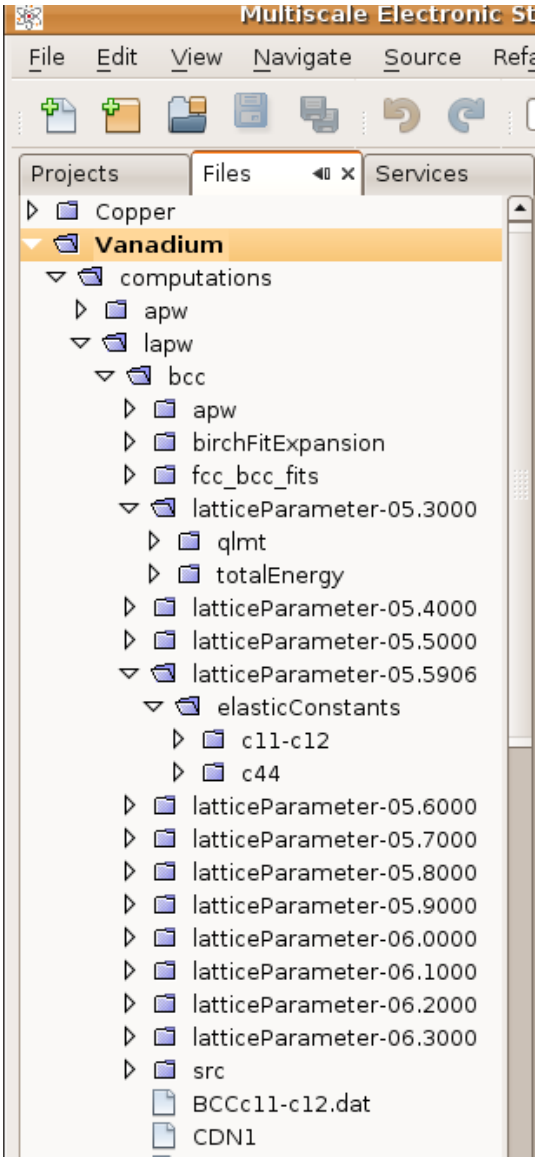

Figure 45: Computations results directory structures.

Click on one of the crystalline structures. The application would display the computational results of LAPW. The sub-directory **apw** would exist only if no CDN1 file was provided and would contain the APW computation performed to obtain the initial

CDN1 file. The **brichFitExpansion** sub-directory contains results of expanding the initial total energy curve to possibly include some more points around the equilibrium lattice parameter. It would also contain a number of sub-directories starting with **latticeParameter-** followed by the lattice parameter in bohrs. For these directories, there would be two more sub-directories in them titled **totalEnergy** and **qlmt**, containing respective computational results. However, the equilibrium lattice parameter would contain a sub-directory **elasticConstants** instead of **totalEnergy**, and **qlmt**. The **elasticConstants** sub-directory would further contain two sub-directories **c11-c12** and **c44**, containing respective computational results.

Chapter 6: TBFIT With MESP

Supported Crystalline Structures for TBFIT Computations

MESP supports the APW output of the following crystalline structures for TBFIT computations:

- Body Centered Cubic (BCC)
- Face Centered Cubic (FCC)

Input for TBFIT Computations

By clicking on the .mesp file of TBFIT, MESP provides in the **Editor** section a facility to enter the following quantities for TBFIT computations:

- Minimum and Maximum energy window to perform computations
- Initial parameters file

Once these options are selected, the user must then save the .mesp file for the changes to take effect.

Running TBFIT

Right click on the tbfit.mesp file in the project and click on **Compute**.

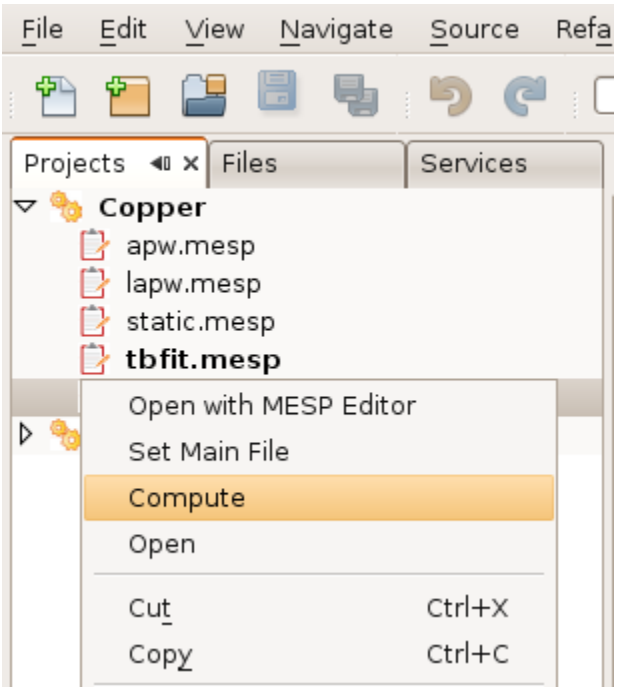

Figure 46: Click on the 'Compute' option of the pop-up menu.

This would run TBFIT with default options. You should notice TBFIT output in the Output area.

Since **tbfit** relies on the output of **apw**, you must have already run **apw** with six bands option in that project before proceeding with **tbfit**. If you want to modify the **tbfit** options, right click on apw.mesp and click on **Open with MESP Editor**. This would open an editor in the **Editor** area.

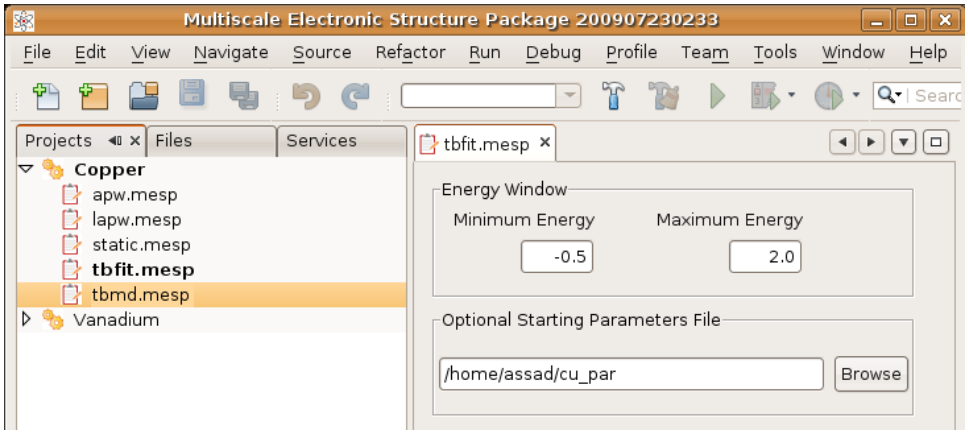

Figure 47: Editing tbfit.mesp file with MESP editor.

You may change **tbfit** options and the click on **File | Save** to save changes. To run **tbfit** gain, right click on apw.mesp file and click on **Compute**.

Inspecting TBFIT Results

Click on the **Files** tab in the **Explorer** area of the application. It would show you the projects that you have opened. Open the one that is being currently working on. Three directories labeled **computations**, **configurations**, and **mespproject**. Open the **computations** directory to reveal the programs that you have run in this project. Open the **tbfit** directory. tbfit starts with total energy and band input from APW and incrementally fits parameters. As it adds on more lattice parameters as input, it increases the range within which the final parameters would perform. At the same time, because there are more constraints to satisfy, the resulting fit would have a larger RMS error. The end-user may find a happy medium between the two in order to maximize utility. This incremental behavior of tbfit is reflected in the directory structure. Each increment causes MESP to

create a **fit-<increment index>-rmsTEError-<total energy RMS error>-rmsBandError-<maximum RMS error while fitting bands>** directory. Each of these directories would contain all the file necessary to re-run the computation. It would also have a **sk_par** file that contains the parameters computed during the run. Every subsequent incremental run takes in the final parameters of the previous run as starting parameters for the new on.

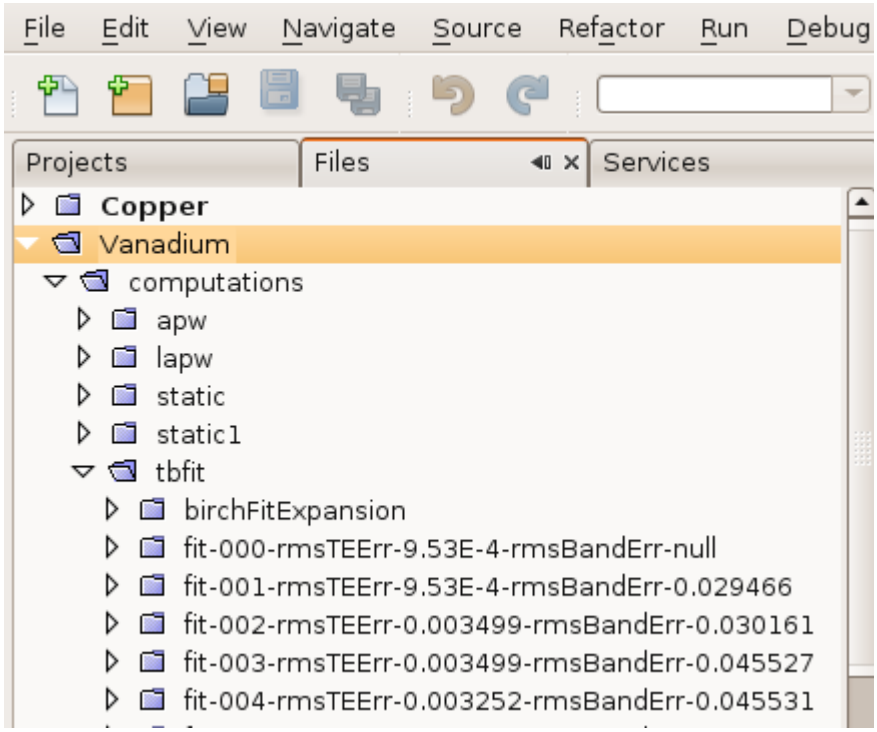

Figure 48: Computations results directory structures.

Chapter 7: STATIC With MESP

Supported Crystalline Structures for STATIC Computations

MESP supports the following crystalline structures for STATIC computations:

- Simple Cubic (SC)
- Body Centered Cubic (BCC)
- Face Centered Cubic (FCC)
- Diamond
- Hexagonal Close Pack (HCP)

Input for STATIC Computations

By clicking on the .mesp file of STATIC, MESP provides in the **Editor** section a facility to enter the following quantities for APW computations:

- Estimated lattice parameter for each of the crystalline structures mentioned above. In case of HCP, c/a and volume is requested.
- The range around the estimated lattice parameter to compute total energy. HCP calculation does not need a range, as it takes a different approach and performs a minimizing algorithm.
- Tight Binding parameters file

Once these options are selected, the user must then save the .mesp file for the changes to take effect.

Input to STATIC Program

Out of the box, STATIC needs a space group file, a kpoints file, a parameters file, and an input file known as the SKIN file. MESP supplies the space group file and the kpoints file from its database. If the user does not specify the parameters file, MESP would look for an appropriate parameters file and if it finds it, it would use it. MESP also generates the SKIN file.

For the total energy computation, he SKIN file is generated with lattice parameter evaluation points around an estimated equilibrium lattice parameter. MESP estimates the equilibrium lattice parameter from its database of experimental lattice parameters. If the crystalline structure is different than for which an experimental value exists, MESP estimates the lattice parameter based on the experimental value. The estimated lattice parameter is rounded off to the nearest tenth of a bohr and a range of +/- 0.5 bohr around that estimated point is evaluated. After evaluated all those points, it uses Birch fit to find the equilibrium lattice parameter.

Running STATIC

You would need a parameters file to run static. Right click on static.mesp file and click on **Open with MESP Editor**. This would open up a window in the Editor area.

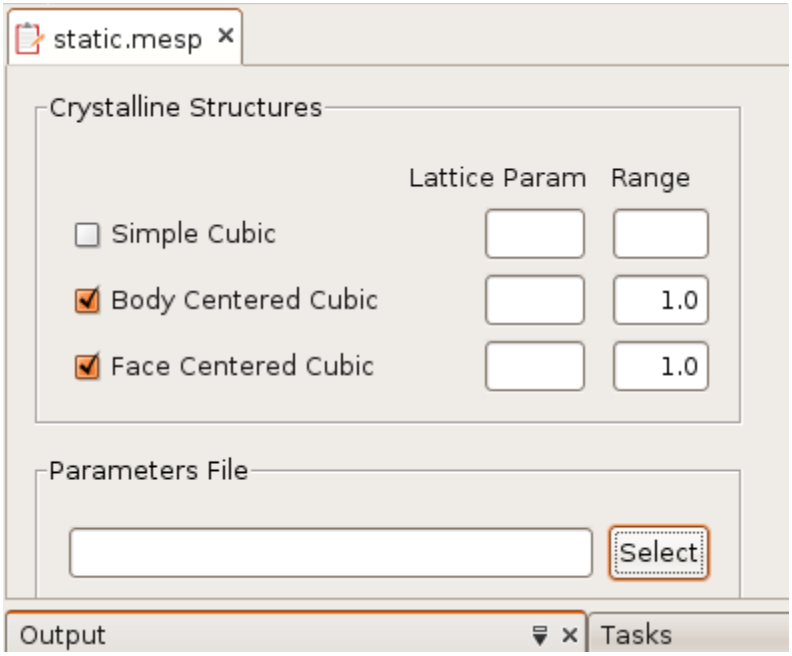

Figure 49: static.mesp in MESP Editor. The blank fields would force MESP to estimate the values by consulting it's internal database.

If you leave the options blank, MESP would guess the lattice parameters from experimental values. It would also look for a suitable parameter file in its database. Click on the **Select** button to open a file system navigator. MESP creates a .mesp directory in your home directory. All projects that you create are placed in this directory. Go to .mesp directory. You may have to type .mesp in the box titled **File Name:** and then click **OK**. Once in .mesp directory, go to the directory that you named your project to be. In that directory, you'd find a mespproject directory that contains a v_par file. This is the parameter file that you want to use to run STATIC.

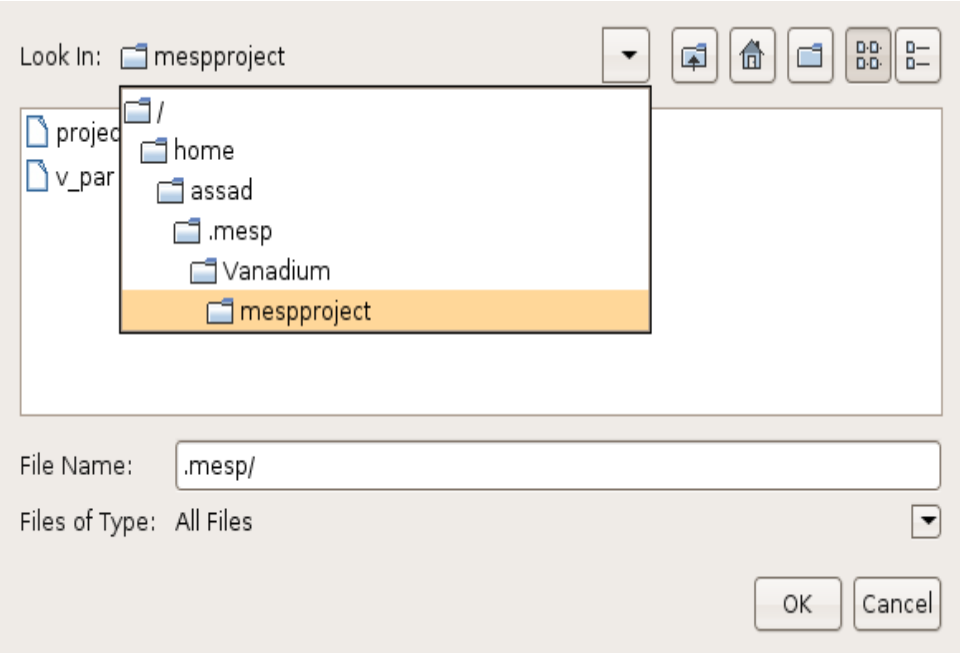

Figure 50: Select the ~/.mesp/Vanadium/mespproject/v_par file.

After selecting the v_par file, click on **OK** to dispose off the dialog box. The full path of the file would appear in the **Parameters File** titled box. Save this by clicking on **File | Save**.

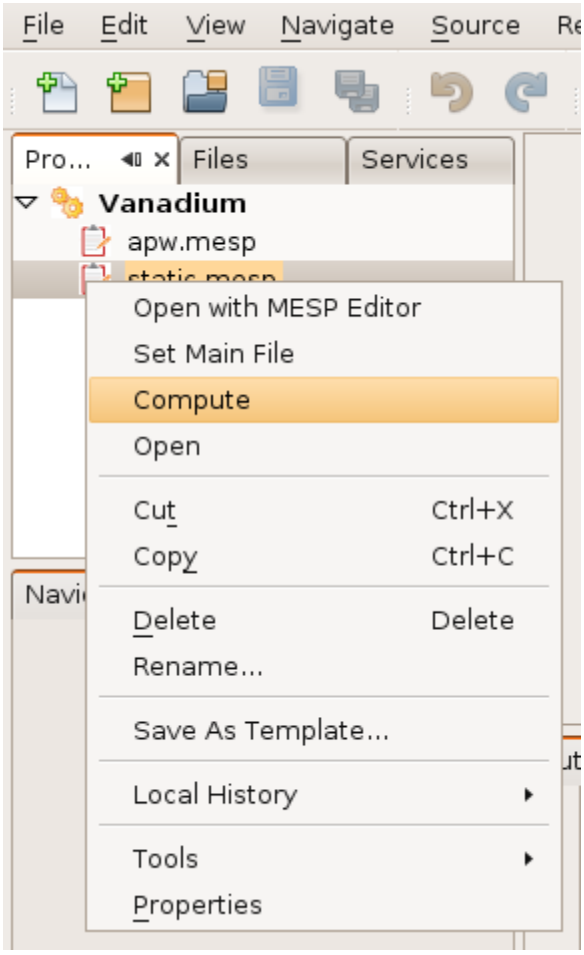

Figure 51: To run STATIC, right click on static.mesp and click on 'Compute'.

Now, right click on static.mesp file and then click on **Compute** menu option in the pop-up menu. You should start to see STATIC output in the **Output** window.

Inspecting STATIC Results

Click on the **Files** tab in the **Explorer** area of the application. It would show you the projects that you have opened. Open the one that is being currently working on. Three

directories labeled **computations**, **configurations**, and **mespproject**. Open the **computations** directory to reveal the programs that you have run in this project. Open the **static** directory, showing the crystalline structures used in the computation. These directories would contain the results of the computations.

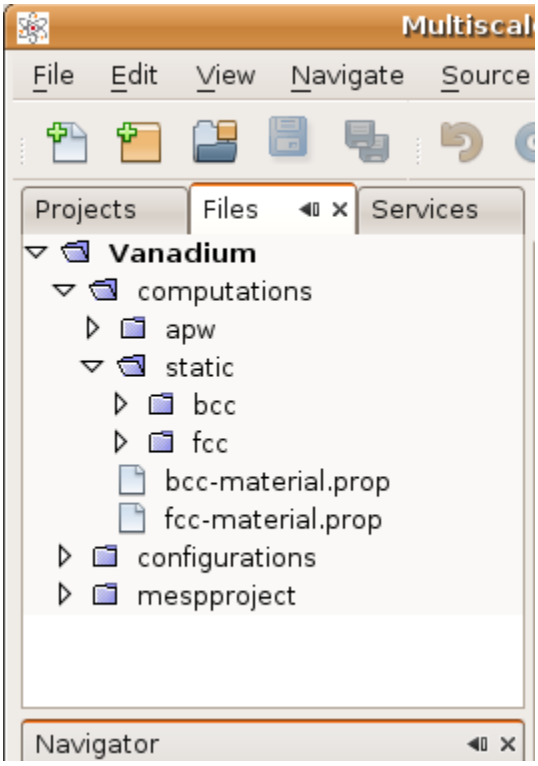

Figure 52: Computations results directory structures.

Click on one of the crystalline structures. The application would display the computational results of STATIC for total energy and for elastic constants. Additionally, it would show directories for density of states calculations (**dos**), phonon frequency calculations (**phonons**), and also a directory called **plots**.

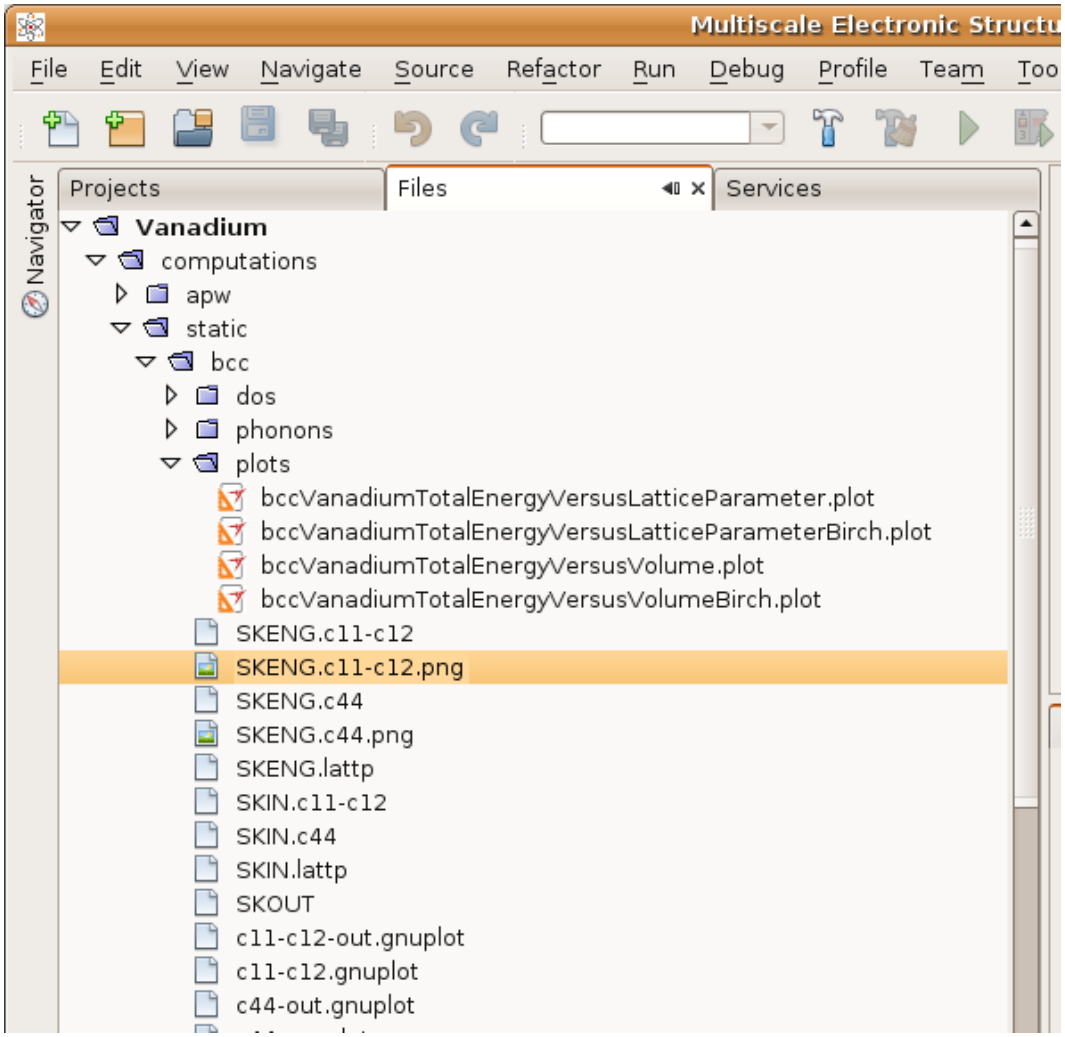

Figure 53: Various directories inside a crystalline structure directory.

Right-clicking and selecting **Open**, or double-clicking on any PNG, JPEG, or GIF file opens the image in the **Editor** area.

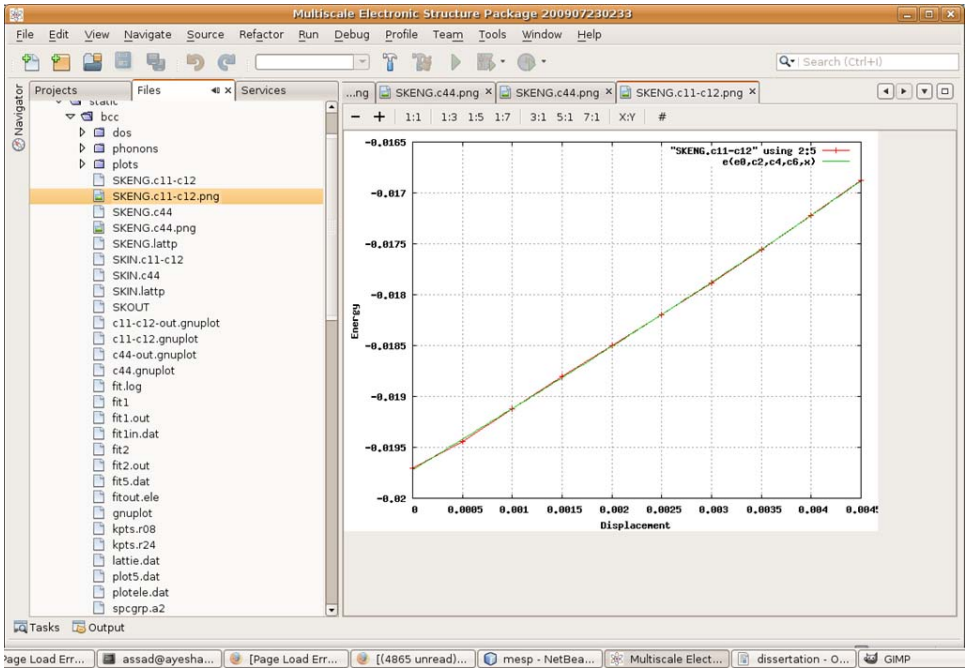

Figure 54: Displaying a .png file in 'Editor' area.

Sample Computations with Copper

Using MESP to execute STATIC produced the following plot of volume vs. total energy for the FCC and BCC computations.

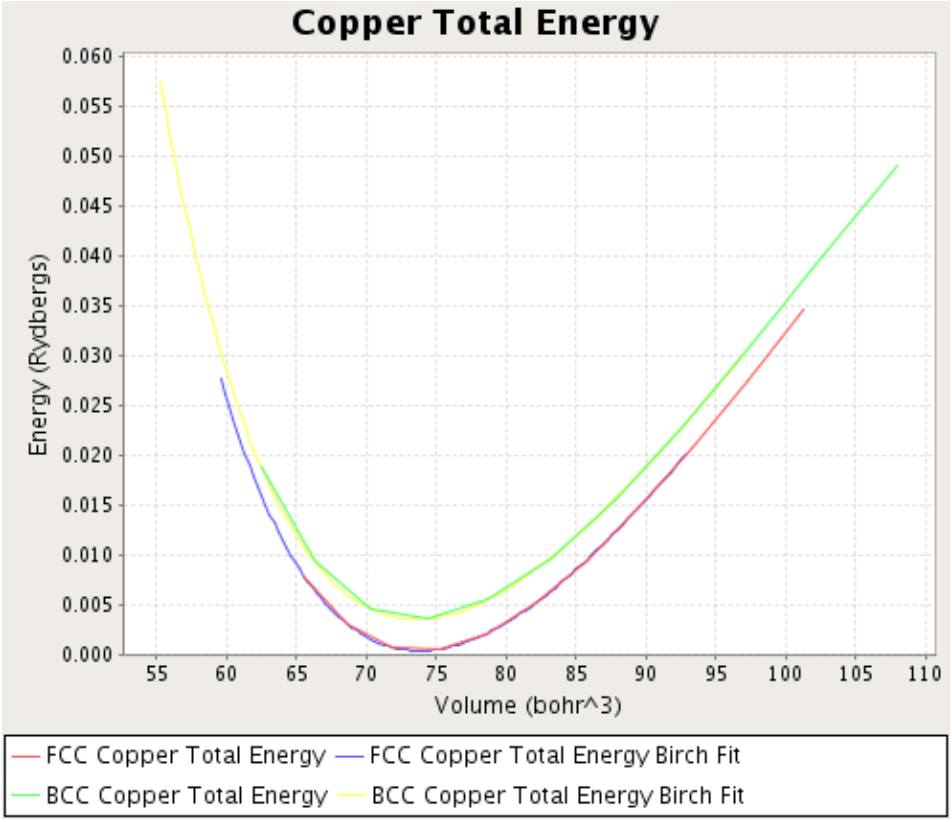

Figure 55: Volume vs. Total Energy for FCC and BCC structures of Copper

This plot shows that Copper prefers FCC structure in ground state as the FCC curve is lower in energy compared to the BCC curve.

The following table summarizes the results of the computations.

Table 4 Lattice Parameters and Bulk Moduli of copper computed via STATIC

Structure	*Lattice Parameter (bohr)*	*Bulk Modulus (GPA)*
BCC	5.28	189.32
FCC	6.66	188.29

The following plot of band energies was produced for FCC Copper in ground state.

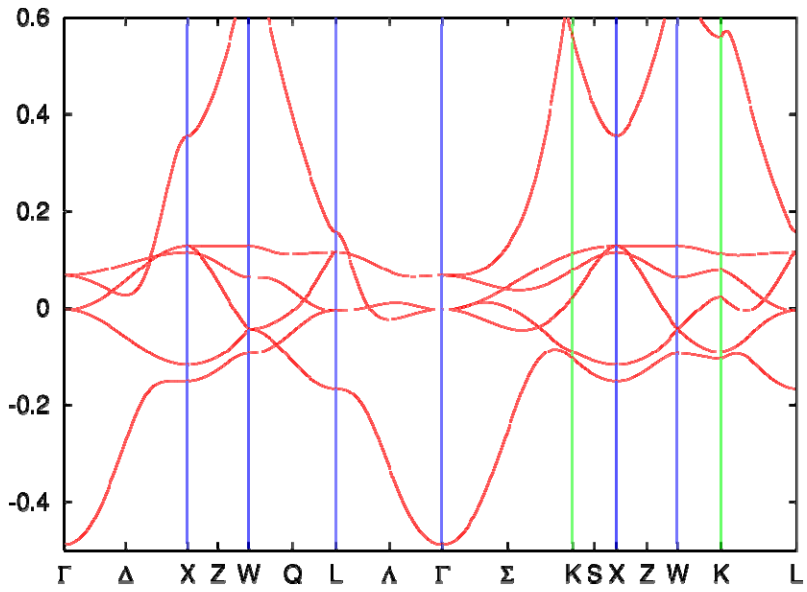

Figure 56: Band energies of FCC Copper. The vertical axis represents the energy in Rydbergs. The horizontal axis has points of high symmetry in a BCC crystalline structure.

The density of states (DOS) plot of FCC Copper in equilibrium lattice parameter is presented below:

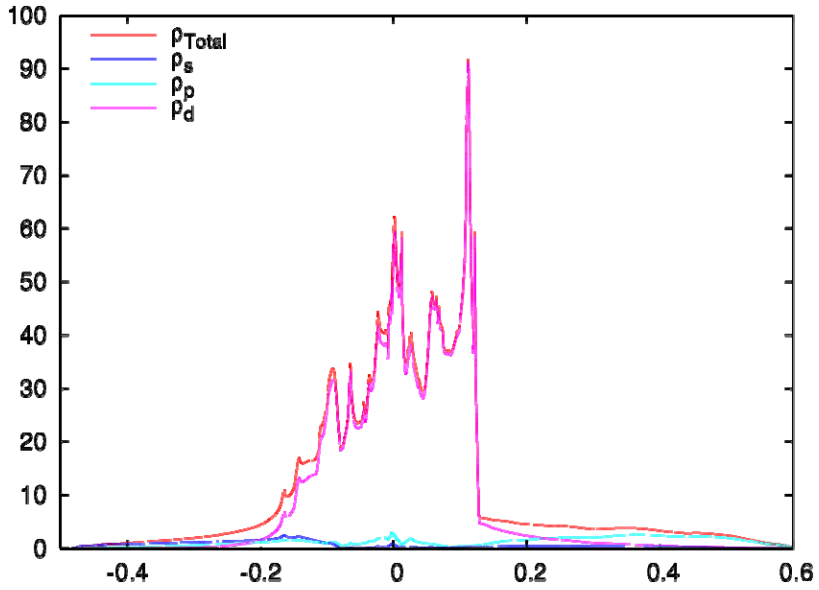

Figure 57: Densities of State (DOS) plot of FCC Copper at equilibrium lattice parameter. The horizontal axis represents the total energy in Rydbergs and the vertical axis is the density of states.

Sample Computations with Vanadium

Using MESP to execute STATIC produced the following plot of volume vs. total energy for the FCC and BCC computations.

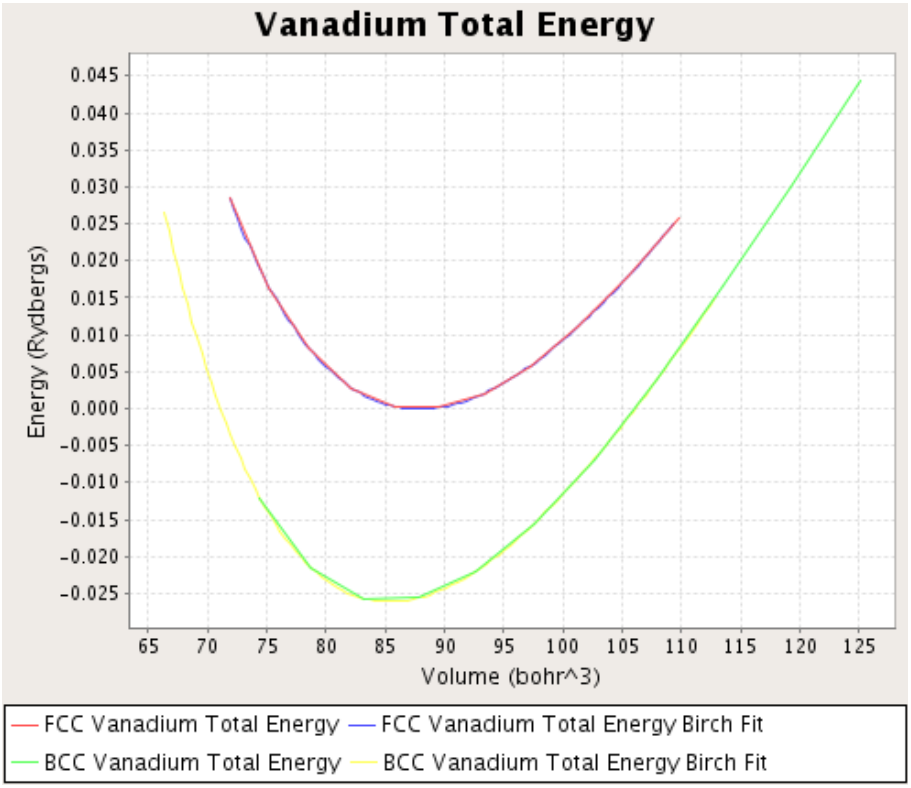

Figure 58: Total Energy vs. Volume for FCC and BCC structures of Vanadium

The following table summarizes the results of the computations.

Table 5 Lattice Parameters and Bulk Moduli of Vanadium computed via STATIC

Structure	*Lattice Parameter (bohr)*	*Bulk Modulus (GPA)*
BCC	5.55	228.89
FCC	7.06	204.62

TB-STATIC produced the following plot of band energies.

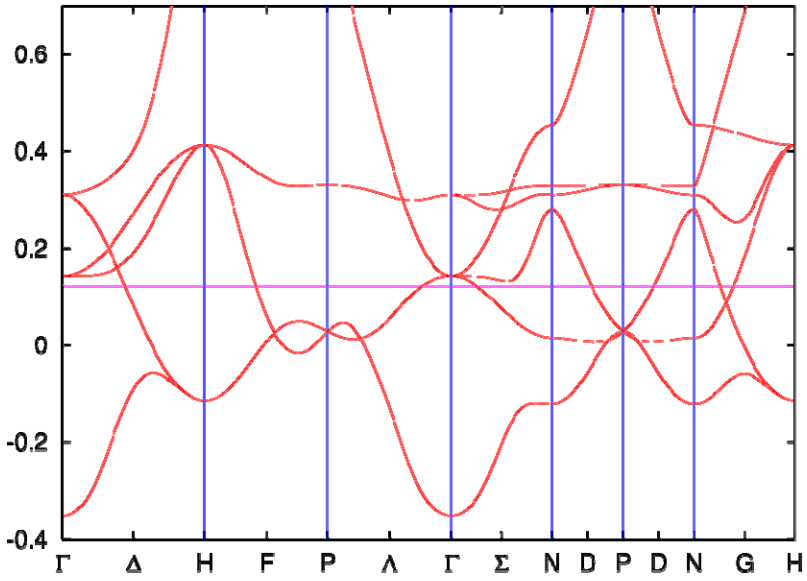

Figure 59: Band energies of BCC Vanadium at equilibrium lattice parameter. The horizontal pink line represents the fermi energy. The vertical axis represents the energy in Rydbergs. The horizontal axis has points of high symmetry in a BCC crystalline structure.

The densities of states plot is presented below for BCC Vanadium:

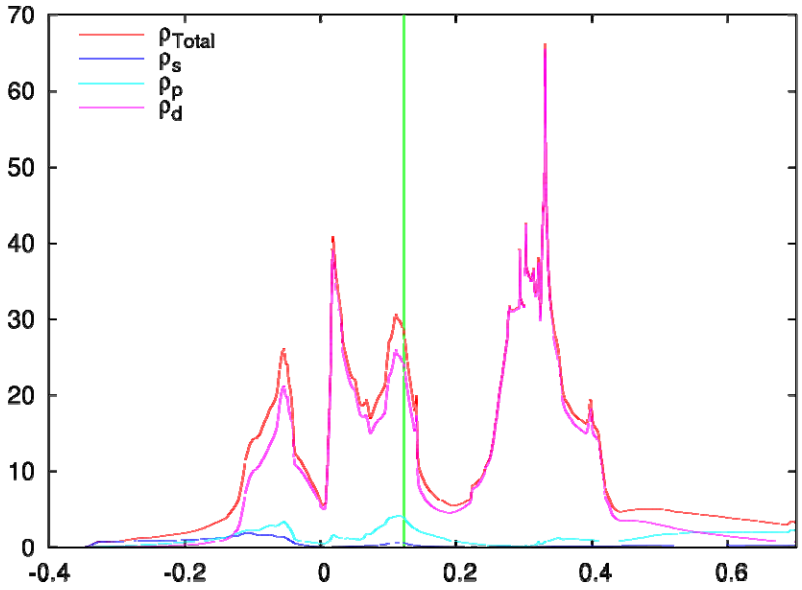

Figure 60: Densities of State (DOS) plot of BCC Vanadium at equilibrium lattice parameter. The horizontal axis represents the total energy in Rydbergs and the vertical axis is the density of states. The green vertical line represents the fermi energy.

Sample Computations with Niobium

Using MESP to execute STATIC produced the following plot of volume vs. total energy for the various crystalline structure computations.

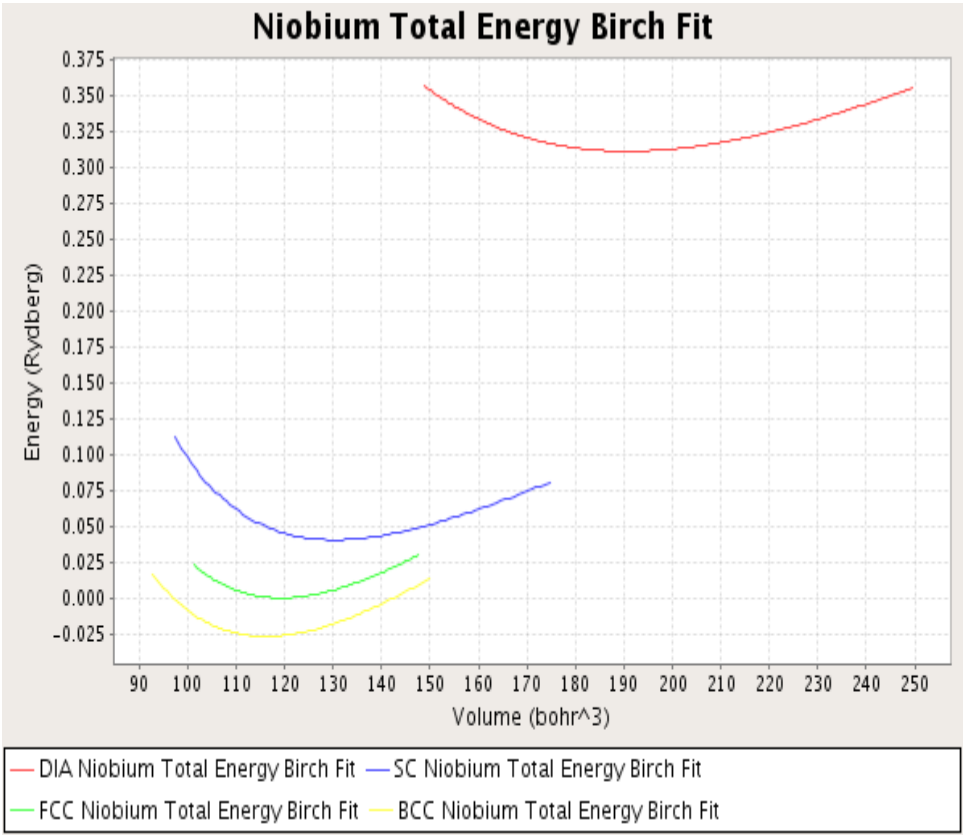

Figure 61: Total energies of, top to bottom, diamond, simple cubic, FCC, and BCC crystalline structures. The plot represents the Birch fit to original data.

The plot above shows that Niobium exists in BCC structure as it has the lowest total energy in that form.

The following table shows some material properties for the different crystalline structures.

Table 6 Lattice Parameters and Bulk Moduli of Niobium computed via STATIC

Structure	*Lattice Parameter (bohr)*	*Bulk Modulus (GPA)*
Diamond	11.51	52.51
SC	5.06	139.89
FCC	7.81	187.55
BCC	6.14	185.05

TB-STATIC also computes band energies. Following is a plot of band energies of BCC Niobium at the equilibrium lattice parameter.

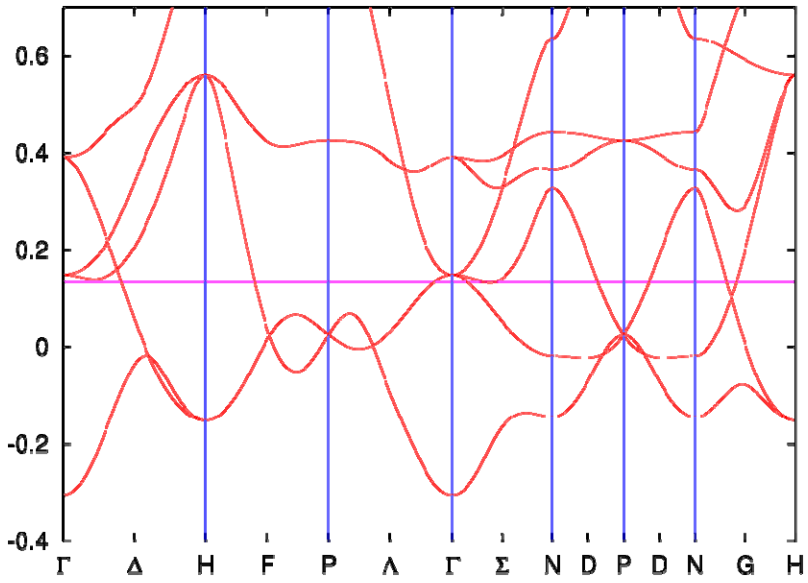

Figure 62: Band energies of BCC Niobium at equilibrium lattice parameter. The horizontal pink line represents the fermi energy. The vertical axis represents the energy in Rydbergs. The horizontal axis has points of high symmetry in a BCC crystalline structure.

The following plot of densities of states (DOS) was also produced by TB-STATIC.

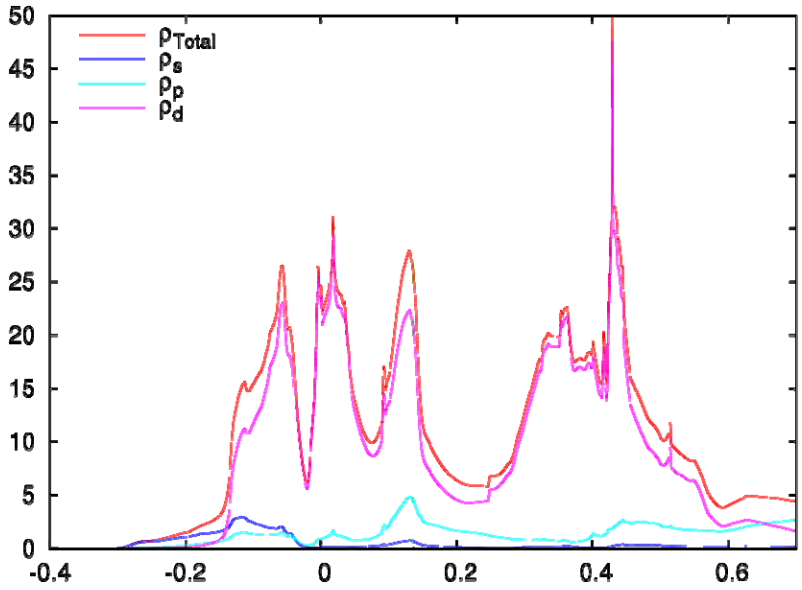

Figure 63: Densities of State (DOS) plot of BCC Niobium at equilibrium lattice parameter. The horizontal axis represents the total energy in Rydbergs and the vertical axis is the density of states. The green vertical line represents the fermi energy.

Chapter 8: TBMD With MESP

Supported Crystalline Structures for TBMD Computations

MESP supports the following crystalline structures for TBMD computations:

- Simple Cubic (SC)
- Body Centered Cubic (BCC)
- Face Centered Cubic (FCC)

Input for TBMD Computations

By clicking on the .mesp file of APW, MESP provides in the **Editor** section a facility to enter the following quantities for APW computations:

- Lattice parameter for each of the crystalline structures mentioned above
- Parameters file
- The starting temperature in Kelvins
- The ending temperature in Kelvins
- The increment in temperature in Kelvins
- The number of steps for each temperature
- The step size in femto seconds

- The cell size in x, y, and z directions

Once these options are selected, the user must then save the .mesp file for the changes to take effect.

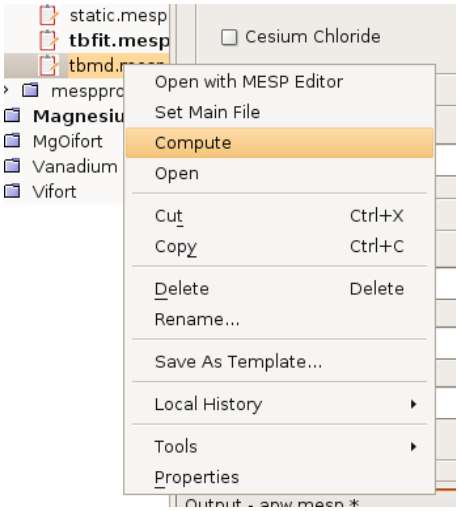

Figure 64: Right click on the .mesp file and click on 'Compute' menu option on the pop-up menu.

Running TBMD

Right click on the tbmd.mesp file and click on **Compute**. This would initiate a TBMD computation and its output would get displayed in the **Output** region of the MESP IDE.

Inspecting TBMD Results

Click on the **Files** tab in the **Explorer** area of the application. It would show you the projects that you have opened. Open the one that is being currently working on. Three directories labeled **computations**, **configurations**, and **mespproject**. Open the

computations directory to reveal the programs that you have run in this project. Open the **tbmd** directory, showing the crystalline structures used in the computation. These directories would contain the results of the computations.

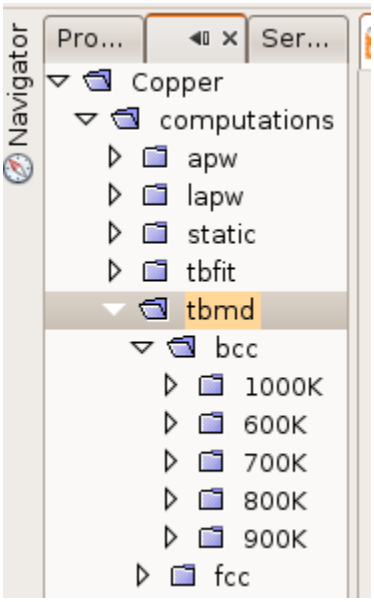

Figure 65: Computations results directory structures.

Click on one of the crystalline structures. The application would display the computational results of **TBMD** for various temperatures in Kelvin. Inside each of the temperature directories, you'd also find a .plot file. Double clicking on this .plot file would display temperature variations during the TBMD simulation.

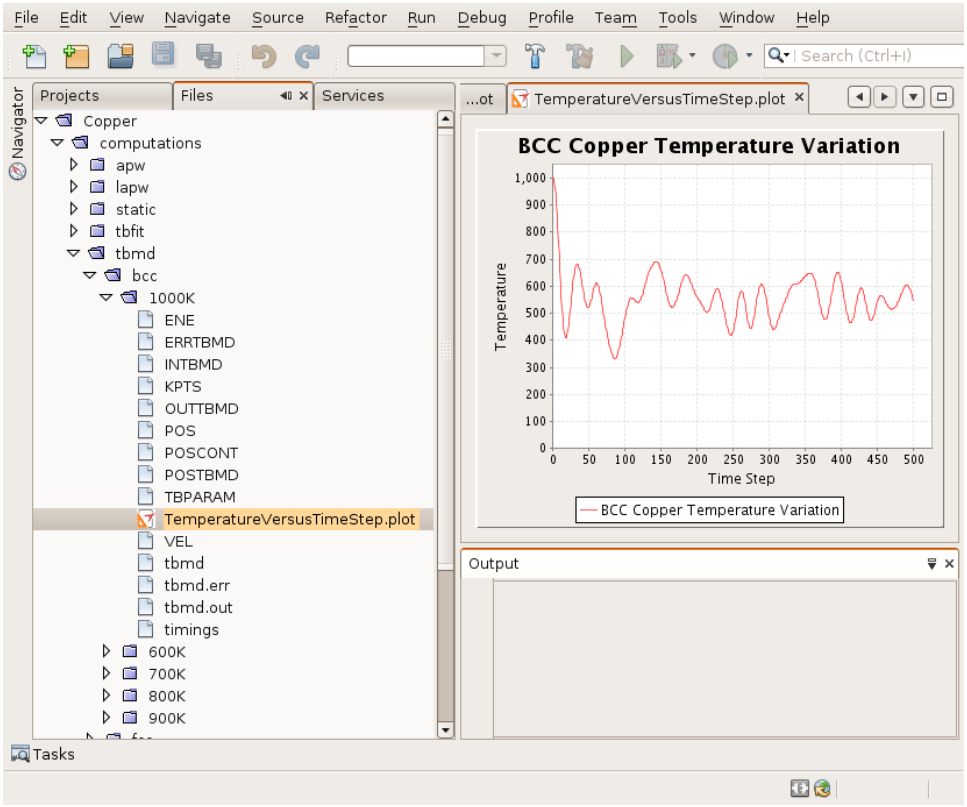

Figure 66: Various directories inside a crystalline structure directory and a sample temperature variation plot.

Sample Computations with Copper

Using MESP to execute TBMD produced the following plots of temperature variations for the FCC and BCC computations.

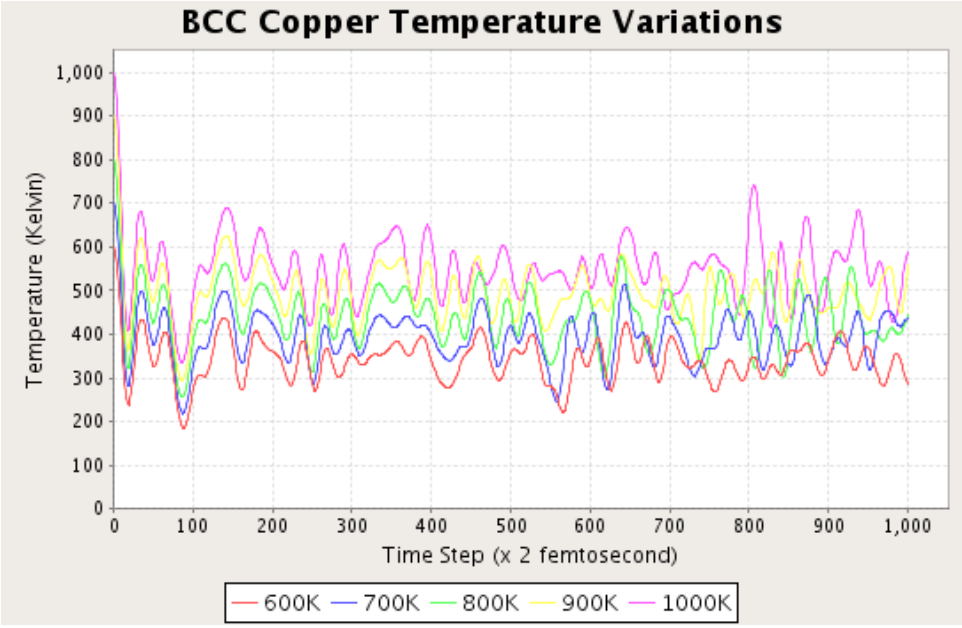

Figure 67: Each plot represents a different starting temperature.

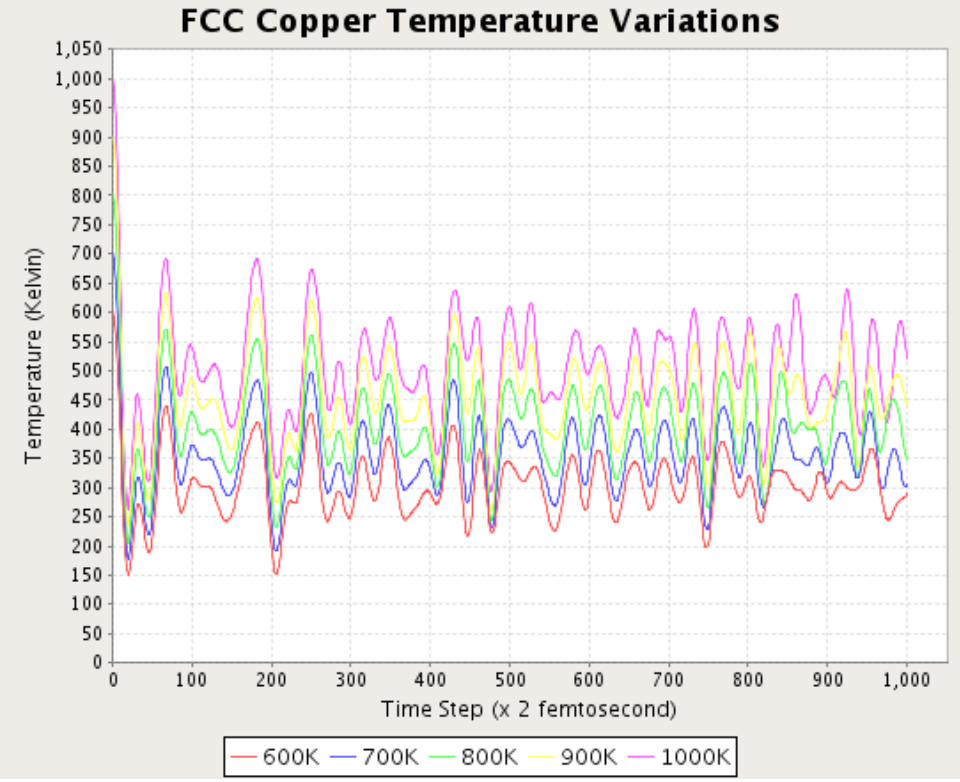

Figure 68: Each plot represents a different starting temperature.

Sample Computations with Vanadium

Using MESP to execute TBMD produced the following plots of temperature variations for the FCC and BCC computations.

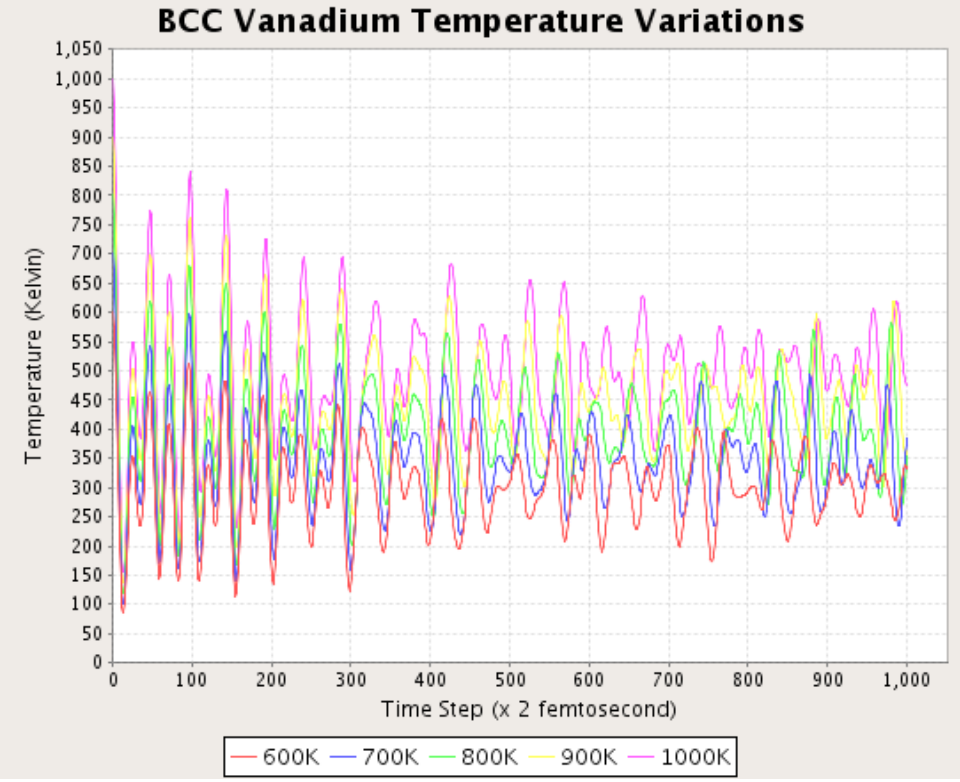

Figure 69: Each plot represents a different starting temperature.

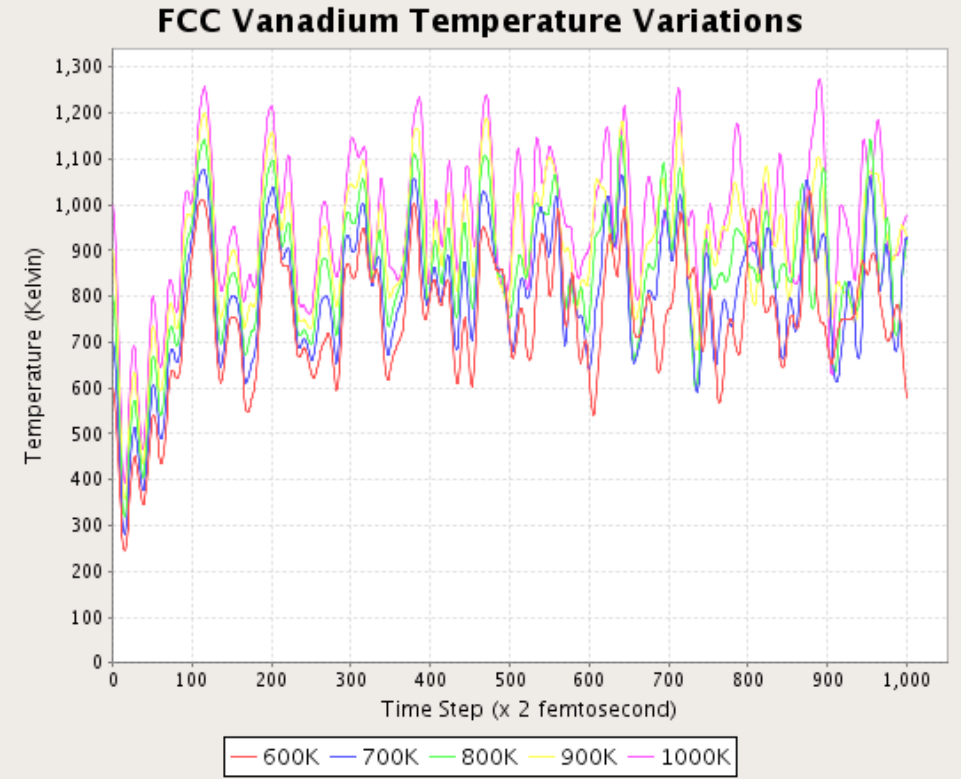

Figure 70: Each plot represents a different starting temperature

Chapter 9: Tight-Binding Fit For Potassium

APW computations were performed for Potassium. Following is a plot of the resulting total energy.

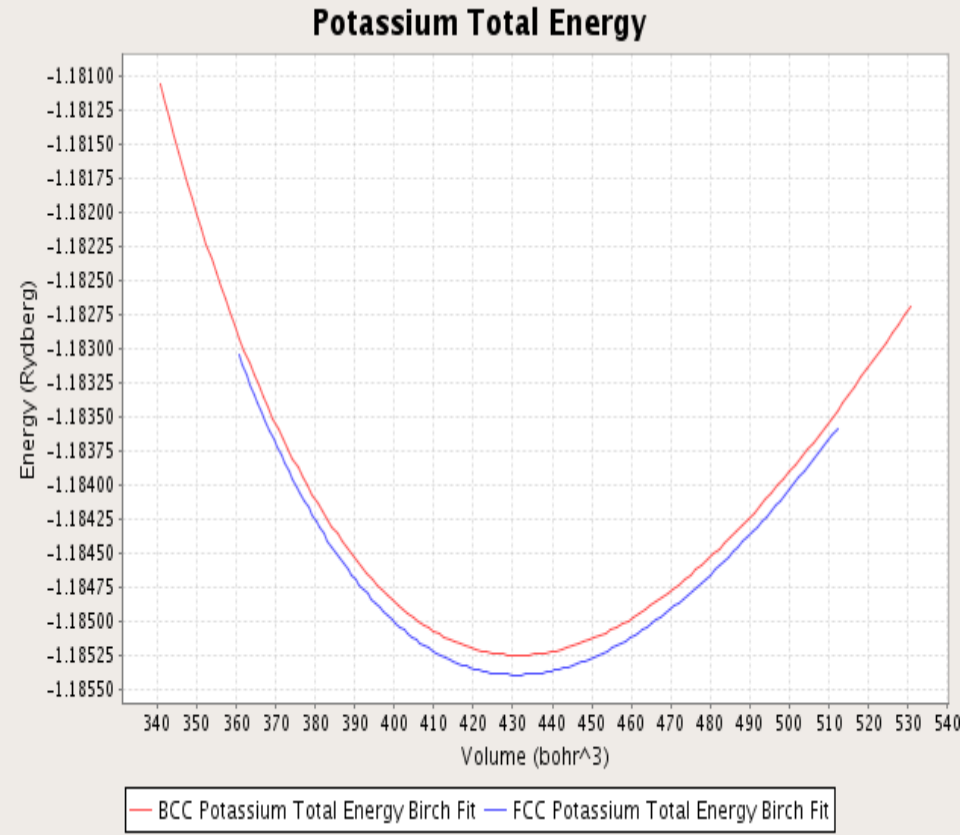

Figure 71: Total energy computed via APW technique.

APW is a first-principles technique based on Density Functional Theory (DFT). In the plot above we see APW showing FCC as the ground state for Potassium. In fact the experimental results tell us that Potassium has BCC is its ground state. So because of the very small energetic difference between the two structures (0.15 mRy), the APW code gives incorrect results. APW found the BCC lattice parameter to be 9.52 bohr (experimental 9.87 bohr [Barrett]) with Bulk Modulus to be 4.5 GPa (experimental 3.66 GPa [Marquardt] [Gerlich]).

The results of these APW computations were used as input to the TBFIT program. The following table presents the fitting errors:

Table 7 RMS errors related to parameters fit for Potassium

RMS Error Type	*Error (mRy)*
Total Energy	0.53
Max Band Energy	21.36

The total energy of BCC structure at equilibrium lattice parameter was subtracted from total energies of both structures before fitting the tight-binding parameters. The total energy shown in the plots below reflect this choice. The resulting tight-binding parameters were used by STATIC to determine various quantities and plots presented below.

Ground State

The following plot generated from the tight-binding parameters shows that the Face Centered Cubic (FCC) is the preferred crystalline structure. Experimental results reflect

that Potassium is actually a BCC metal. The plot below indicates a phase transition from FCC to BCC under pressure.

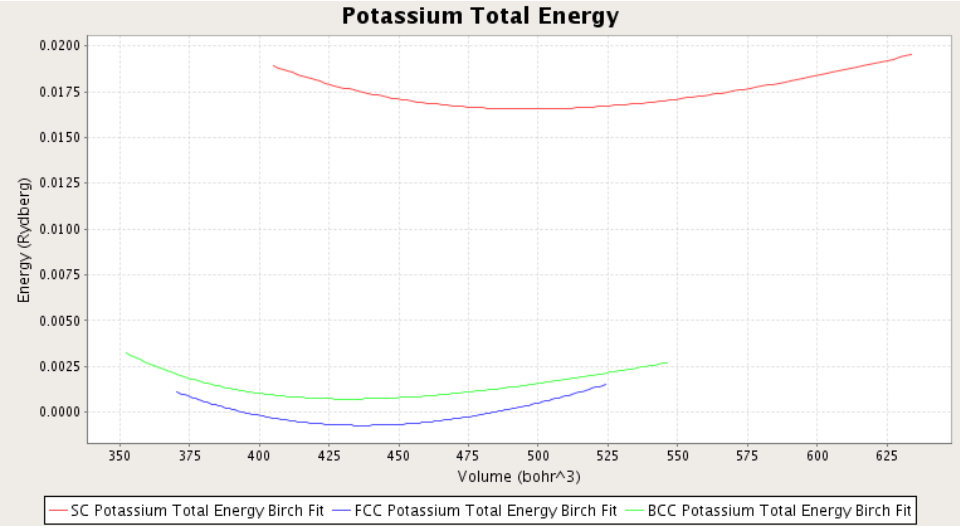

Figure 72: Total energy vs. volume of various crystalline structures using newly-found tight-binding parameters of potassium.

A close-up of the plot above reveals a difference between the equilibrium lattice parameters of FCC and BCC Potassium of around 1.4 mRy.

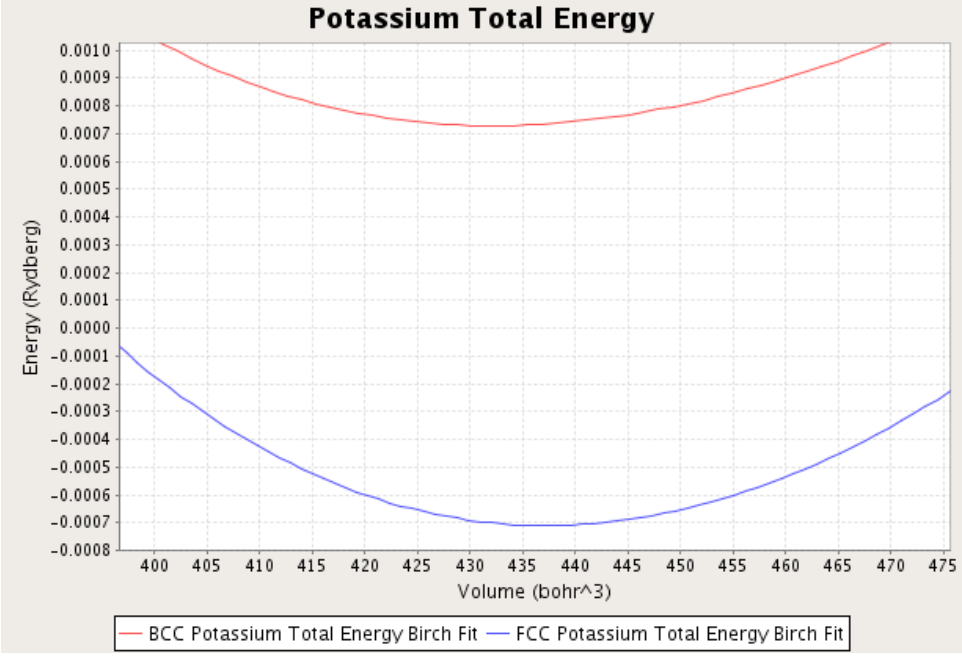

Figure 73: A closeup of total energy versus volume to see the difference in energy.

For the rest of this chapter the BCC structure (as confirmed by experiment) is discussed.

Lattice Parameter

The tight-binding parameters fitted to APW results produced agreement with the STATIC calculations.

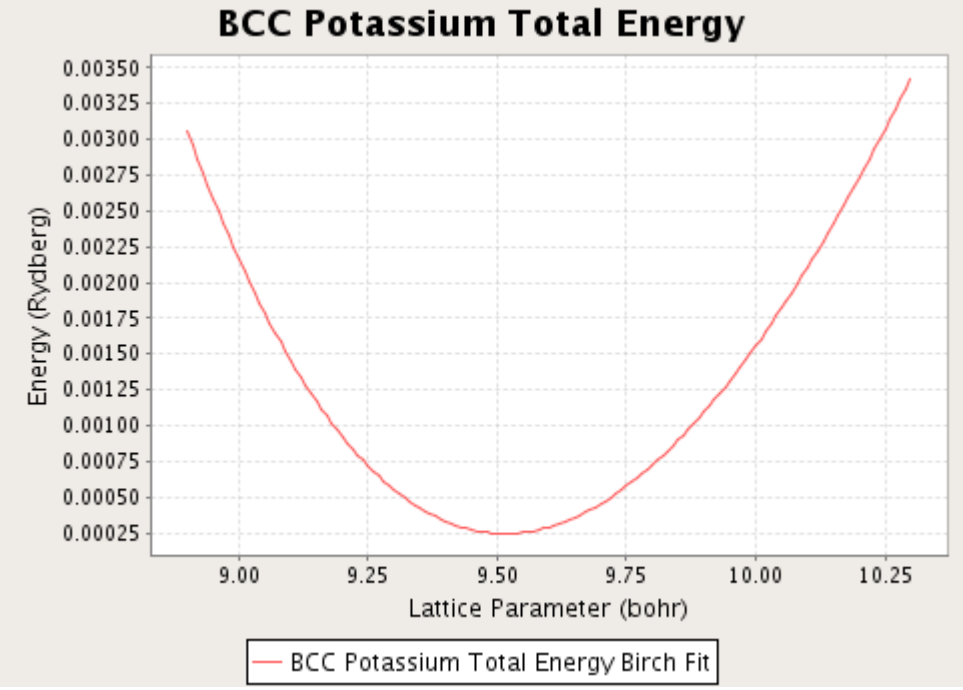

Figure 74: Total energy plot as a function of BCC lattice parameter.

The calculation was performed on BCC lattice parameters from 8.8 bohr to 10.2 bohr with 0.1 bohr increments. The equilibrium point lattice parameter was determined to be 9.52 bohr for BCC structure. That's an absolute error of 0.015 bohr and a relative error of 1.5% with respect to the APW technique.

Barrett [Barrett] reports the lattice parameter of 9.877 bohr (5.225 Angstrom). With respect to the experimental result the STATIC result has an absolute error of 0.357 bohr and a relative error of 3.61%.

Elastic Constants

The fitted plot for C11-C12 is presented below for the BCC lattice:

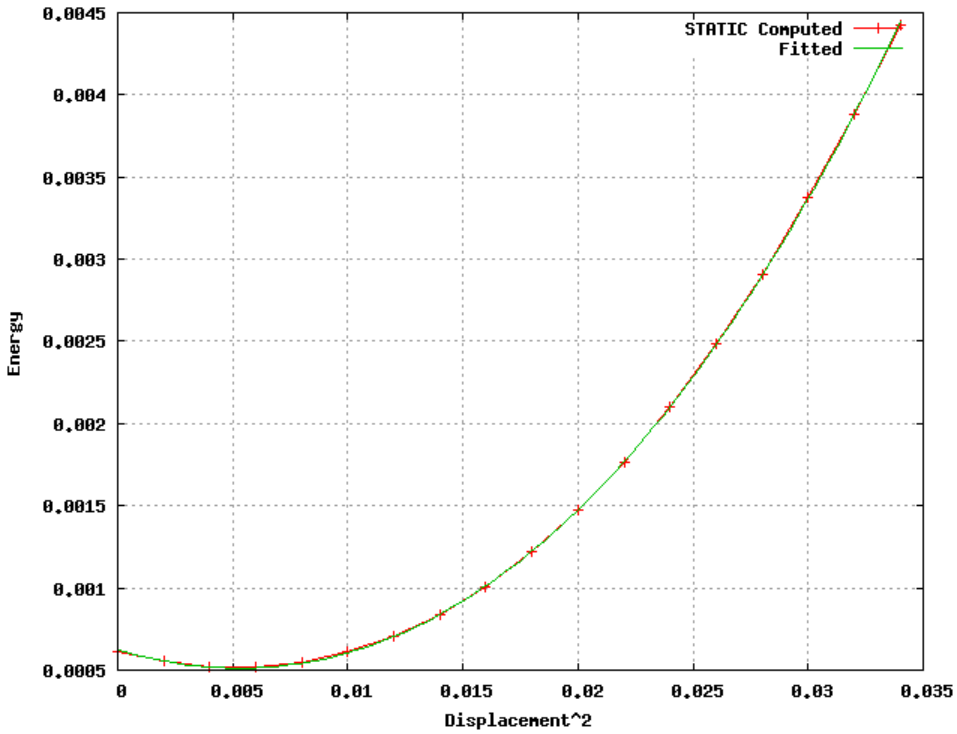

Figure 75: Energy as a function of Orthorhombic strain displacement for the BCC lattice.

The slope of the plot above indicates a very soft lattice, making it difficult to compute the elastic constants.

C11 thus computed was 2.29 GPa, and C12 thus computed was 3.70 GPa.

The fitted plot for C44 is presented below:

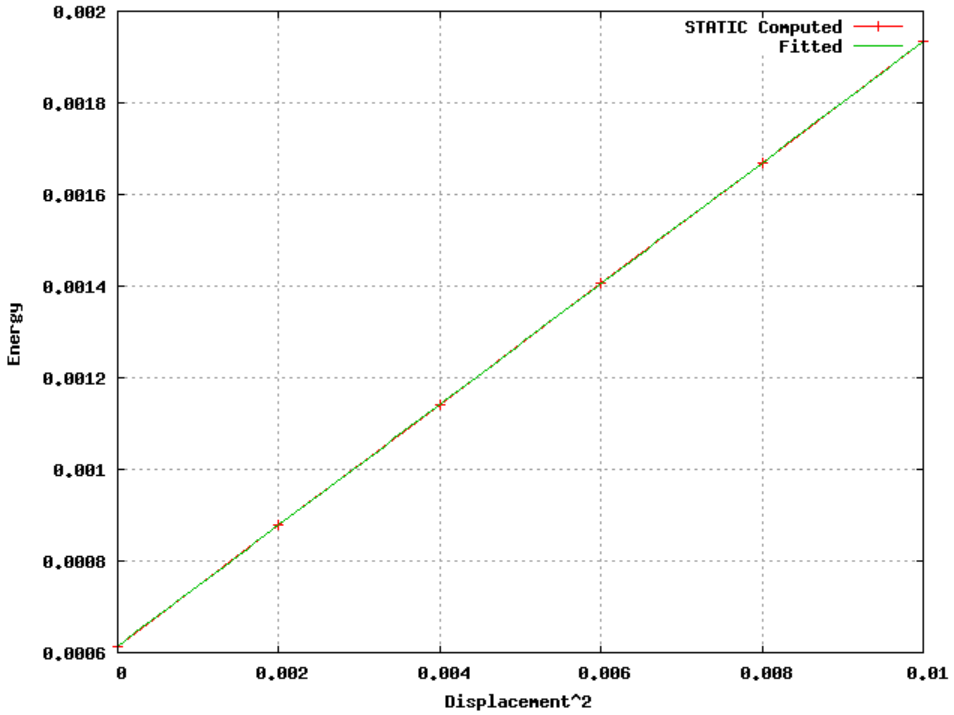

Figure 76: Energy as a function of displacement due to monoclinic strain on BCC K structure to determine C_{44}.

C_{44} thus computed was 8.99 GPa.

Comparison with Experimental Results

Table 8 Comparison of elastic constants and bulk modulus computed via STATIC with the experimental results

Quantity	*NRL-Tight Binding (GPa)*	*Experimental at 4 K (GPa) [Marquardt] [Gerlich]*
C11	2.29	4.16
C12	3.70	3.41
C44	8.99	2.86
Bulk Modulus	3.23	3.66

The relative error in the elastic constants above is large because Potassium is a soft alkali metal and it is very difficult to compute these quantities for such material. The absolute error is comparable to those found for the transition metals, where these quantities are generally in hundreds of GPa.

Energy Bands

The energy bands of the BCC structure are plotted below with a different set of tight-binding parameters. This set of tight-binding parameters had a lower max RMS band error of 18 mRy and was thus chosen to produce the bands below:

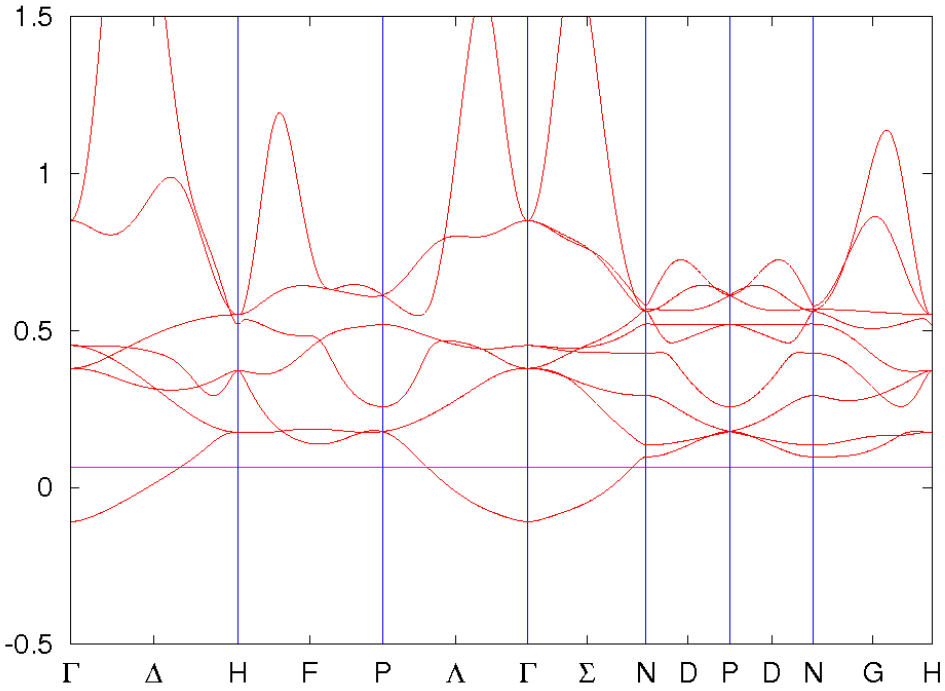

Figure 77: Energy bands of K in BCC structure using tight-binding parameters

The Fermi energy is crossed over by the bands, indicating that Potassium is a metal.

For comparison, the bands produced using the APW technique (from which the tight-binding parameters were obtained) are presented below:

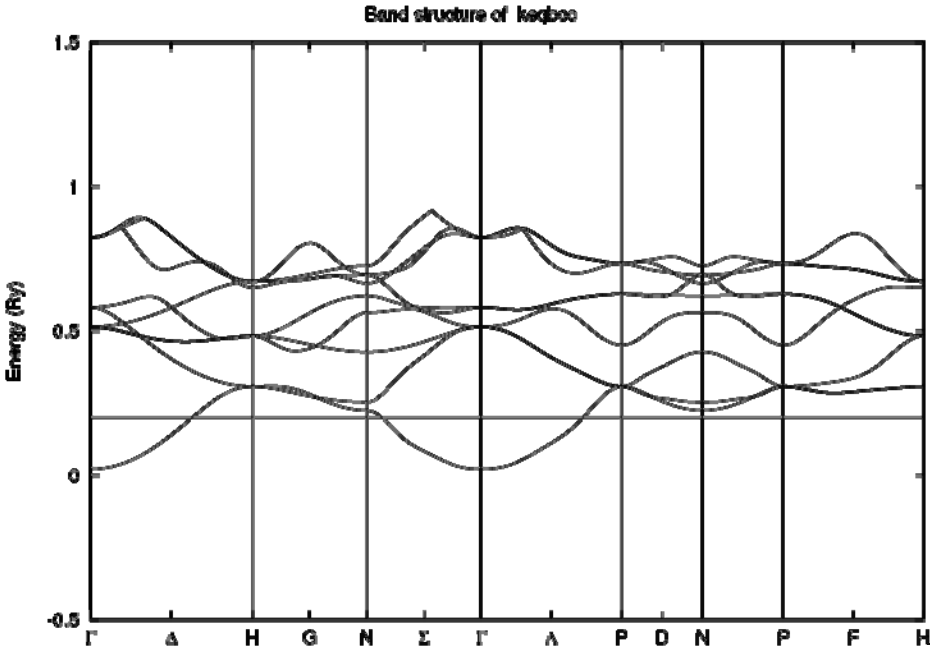

Figure 78: Energy bands of K in BCC structure via the APW technique

When comparing the bands from the two techniques, notice that the high symmetry points on the horizontal axis are listed is a slightly different order. The higher energy bands that have at least a portion of it higher than the maximum of 1.5 Rydbergs were omitted in the APW technique. After accounting for these two differences, the two plots are very similar to each other.

Density of States

The density of states of Potassium in BCC structure is plotted below using the same set of tight-binding parameters that produced the bands plot above.

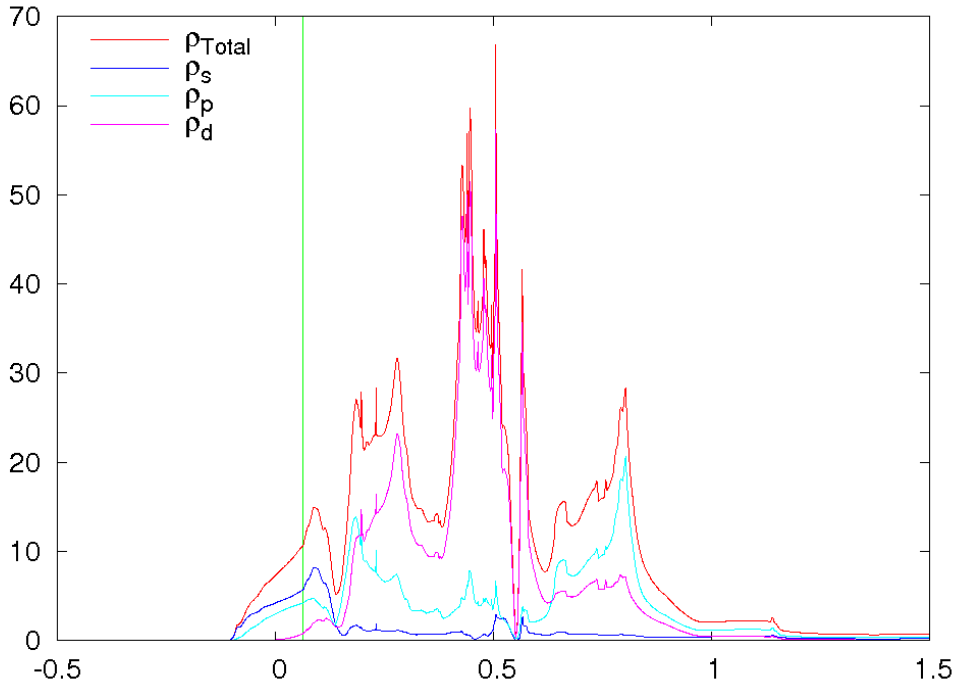

Figure 79: Density of States (DOS) of Potassium in BCC structure using tight-binding parameters

For comparison, the density of states obtained using the APW technique is also plotted below:

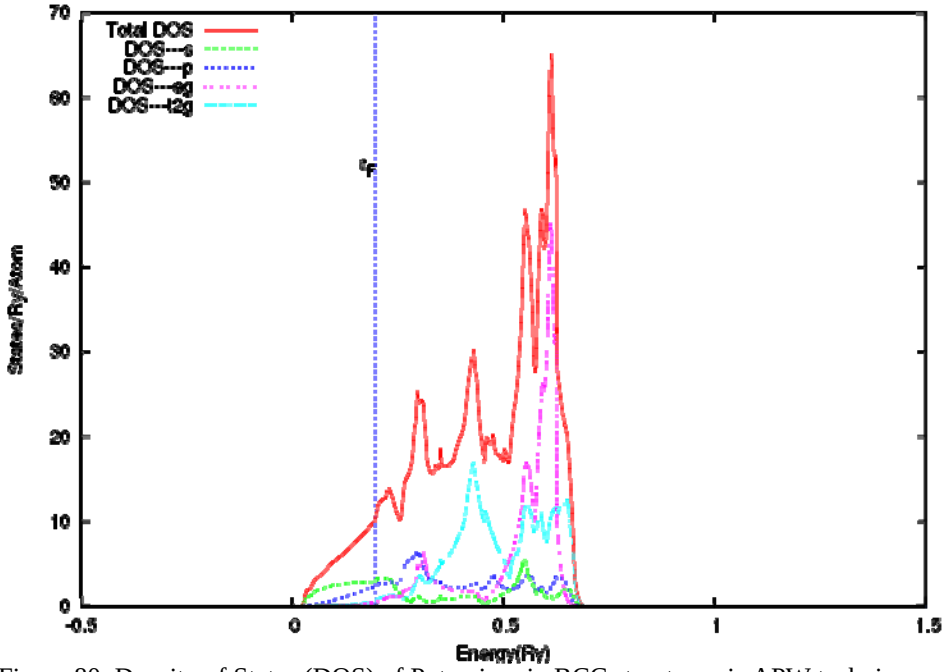

Figure 80: Density of States (DOS) of Potassium in BCC structure via APW technique.

The sharper drop in the density of states around 0.7 Rydberg is due to the fact that higher energy bands that crossover the max range are ignored altogether in the APW technique. Again the two plots are quite similar, after accounting for this difference.

BCC Phonon Frequencies

The phonon frequencies for the BCC structure were computed as following:

Table 9 Phonon frequencies of BCC Potassium computed via STATIC using the fitted parameters

Name	*Value (Hz)*
H	4.02
P	3.19
N2	2.71
N3	4.29
DT1	2.29
DT5	2.92

The N4 frequency was determined to be imaginary: *i*0.77.

Tight-Binding Molecular Dynamics

The tight-binding parameters were also used in a Molecular Dynamics setting. The initial temperature setting starting from 50K through 250K was used. The experimental melting point of potassium is 336.53 K. The tight-binding parameters fail during TBMD runs of 300K or higher. The temperature variations for various starting temperatures are depicted below. The volume was kept constant at 432.2 bohr^3, corresponding to the lattice parameter of 9.52 bohr. A cell of 3 x 3 x 3 atoms (27 atoms) was used. The volume of the supercell was 1,712.42 bohr^3,

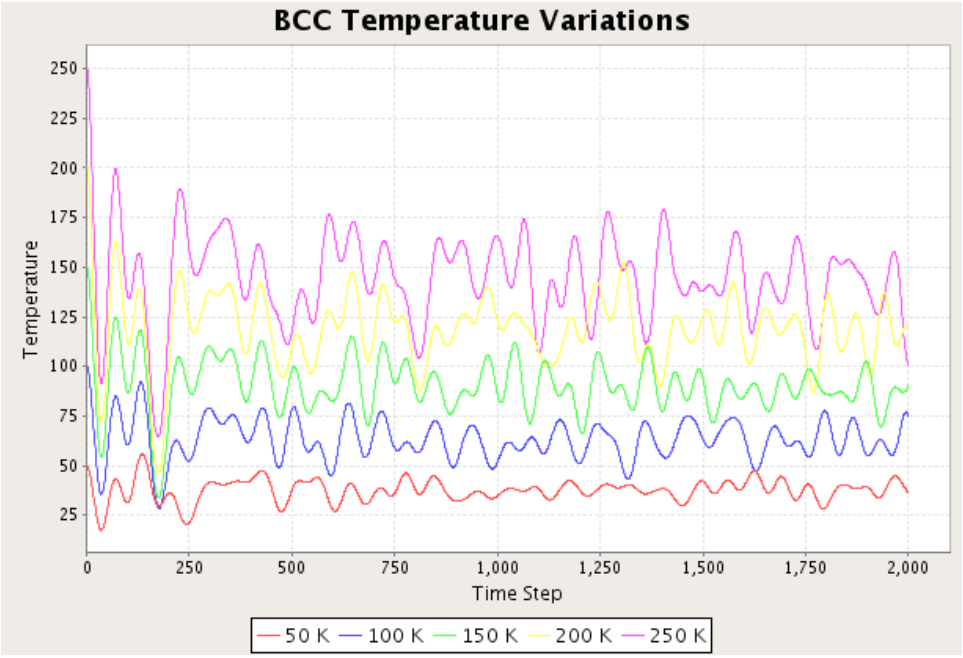

Figure 81: Temperature variations from different starting temperatures for BCC Potassium at 9.52 bohr fixed lattice parameter (fixed volume).

Chapter 10: Computations With Magnesium Oxide (MgO)

MESP can also be used to determine material properties of a diatomic material using APW. About 37.8% of earth's mantle is estimated to be of MgO. APW computations were performed to determine the enthalpies of Magnesium Oxide (MgO) for NaCl and CsCl structures and the pressure needed to transition from one structure to another.

Structural Comparison

The following plot of total energy as a function of volume for NaCl and CsCl structure, obtained from APW, shows that the NaCl structure has lower energy at equilibrium point and is thus the preferred structure.

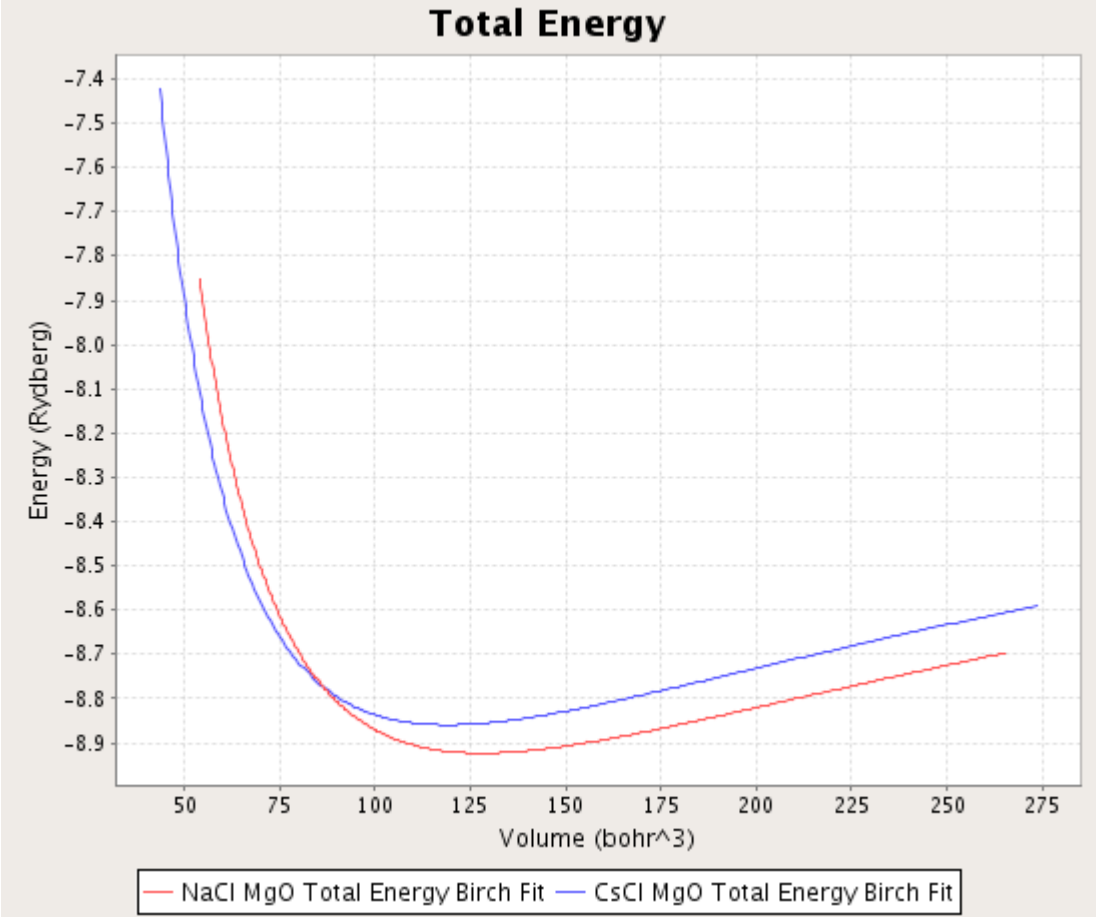

Figure 82: Energy as a function of volume for NaCl and CsCl structures of MgO.

The NaCl lattice parameter thus was determined to be 7.99 bohr.

Also, the enthalpy calculations indicate the same with the NaCl structure remaining stable even under pressure.

Enthalpy is computed by:

$H = E + PV$

where H is enthalpy, E is Energy, P is pressure, and V is volume.

The curve above is used to compute the pressure using:

P = - E'(V)

This yields the enthalpy of the system at the various volumes.

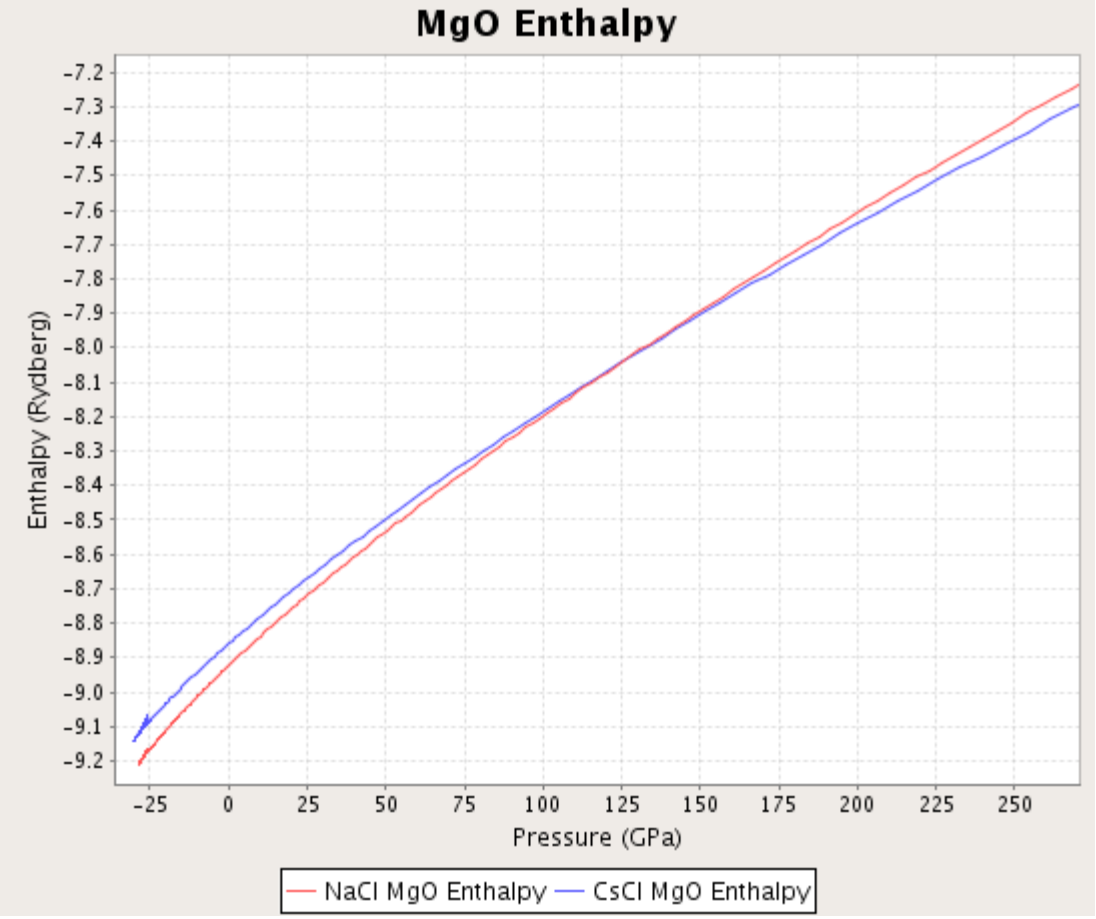

Figure 83: Enthalpy as a function of Pressure for NaCl and CsCl structures of MgO.

The plot above shows that MgO crystallizes in NaCl under normal conditions, but changes into CsCl under high pressure.

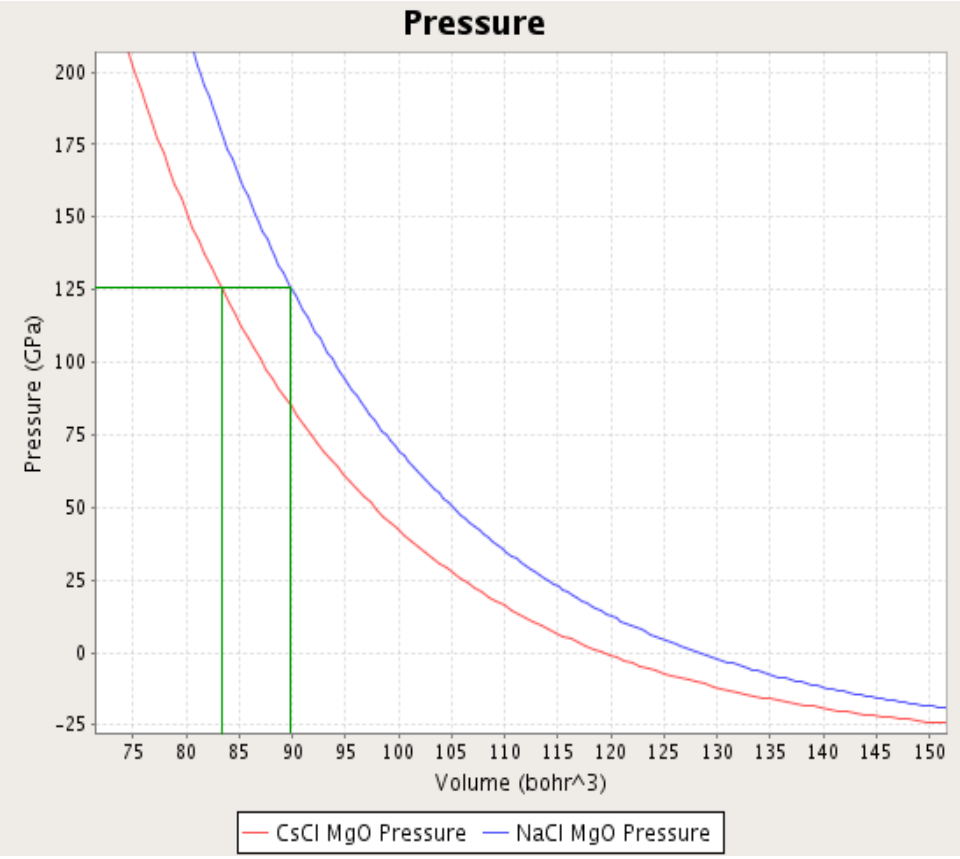

Figure 84: Pressure as a function of volume for the two structures. The horizontal line shows the transition pressure of 126 GPa.

The structural volume contracts when transitioning from NaCl to CsCl structure. The following plots show pressure as a function of volume for the two structures.

A close up of the above plot is shown below:

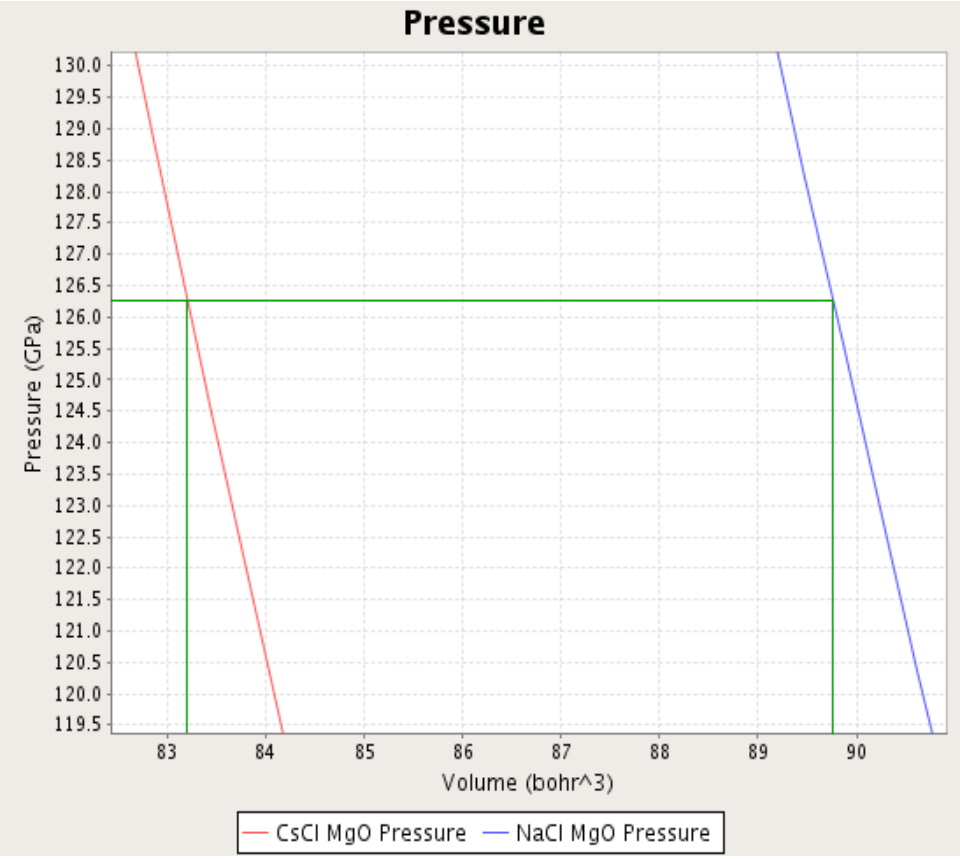

Figure 85: A close up of pressure as a function of volume for the two structures. The horizontal line shows the transition pressure of 126.25 GPa.

This shows that as MgO transitions from NaCl, under (126.25 GPa) pressure, to CsCl, it changes its volume from about 89.8 bohr^3 to 83.22 bohr^3 – a 7.32% contraction.

Comparison with Other Studies

The results thus computed with APW are in agreement with experimental results and other computational studies. As Kittel has indicated, the preferred lattice structure for MgO is NaCl with a lattice parameter of 4.2 Angstrom (7.94 bohr) [Kittel pg 14].

MgO is studied computationally by several scientists. There are studies conducted using LAPW [Mehl] and also a Green's function methodology with help of APW technique [Klein].

Mehl et. al. [Mehl] also computed enthalpies of the two structures and determine NaCl to be stable until 510 GPa and for pressures higher than it, CsCl is preferred. These calculations were based on LAPW technique. The plot is presented below from [Mehl]:

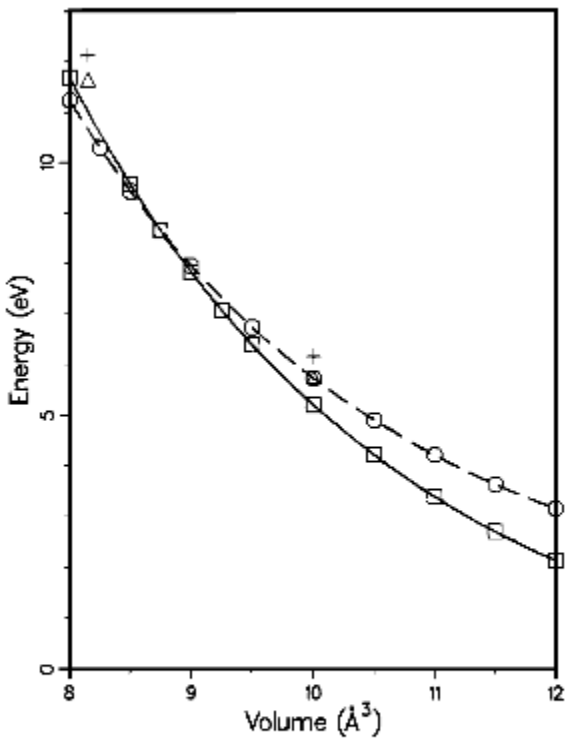

Fig. 4. LAPW energy versus volume for MgO. As in Figure 1, our B1 calculations are represented by the squares, our B2 calculations by the circles, and the curves represent third-order Birch fits to the data. The triangles indicate the energy of the B8 (NiAs) phase when the O ion is on the arsenic site, and the crosses indicate when the Mg ion is on the arsenic site.

Figure 86: Comparison of phase transition with Mehl et. al. [Mehl] study with LAPW technique.

Karki et. al. [Karki] also computed enthalpies of the two structures and determine NaCl to be stable until 451 GPa and for pressures higher than it, CsCl is preferred. These calculations were not based on APW technique. The plot is presented below from [Karki]:

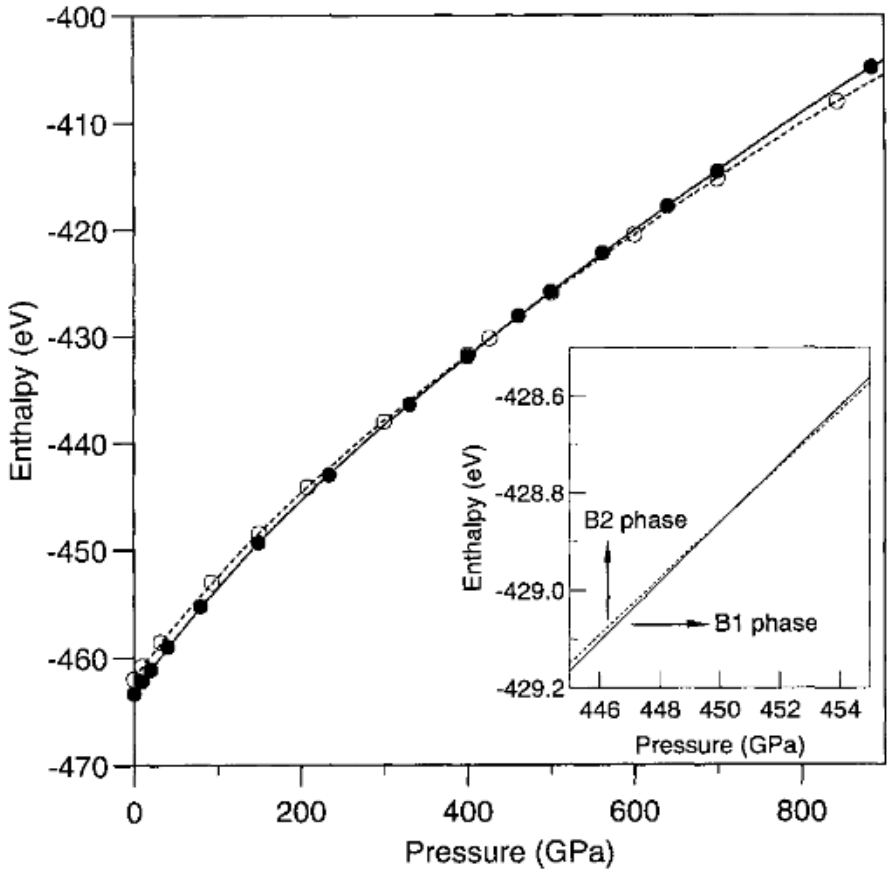

FIGURE 2. The B1-B2 phase transition in MgO. The solid line (solid circles) and dashed line (open circles) show the calculated zero-temperature free energies as a function of pressure for the NaCl and CsCl structures of MgO, respectively. The inset illustrates intersection of the curves, giving 451 GPa as the transition pressure.

Figure 87: Comparison of Enthalpies by Karki et. al. [Karki].

Band Structures

The band structures for MgO in NaCl and CsCl crystalline structures were also computed and are presented below:

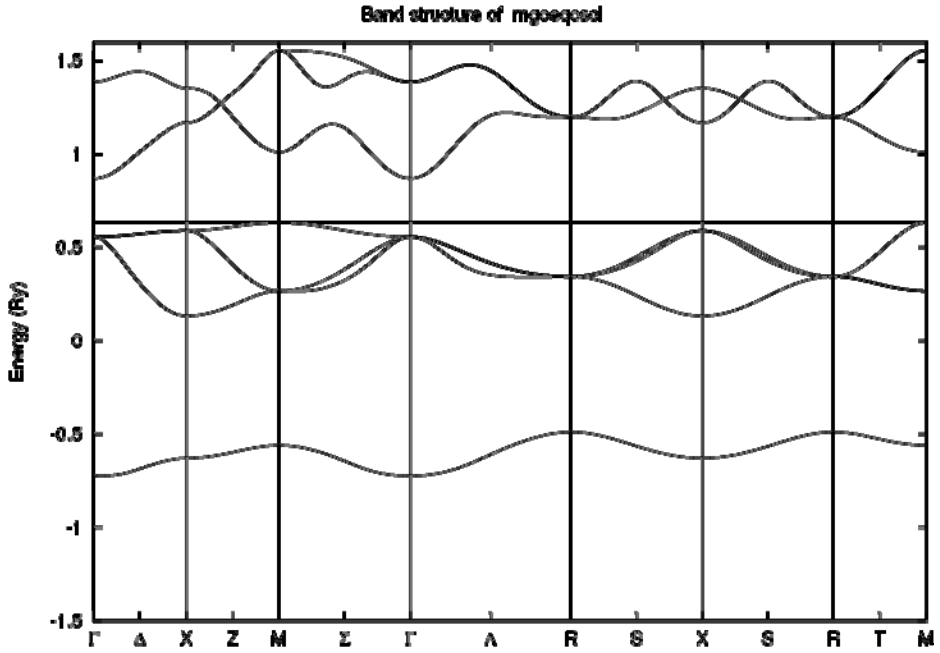

Figure 88: Band structure of MgO in CsCl crystalline structure at equilibrium lattice parameter of 4.91 bohr.

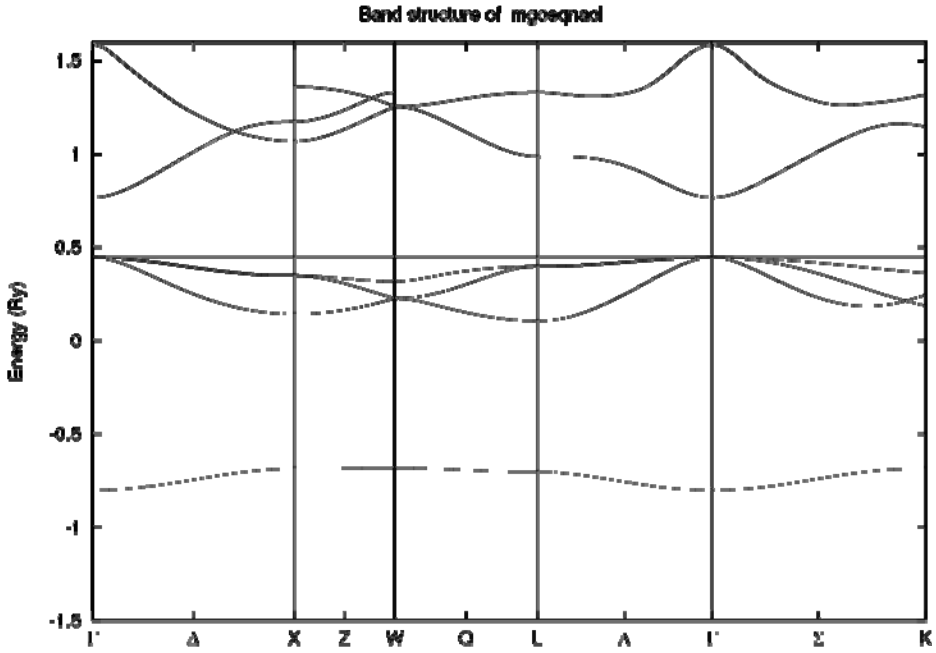

Figure 89: Band structure of MgO in NaCl crystalline structure at equilibrium lattice parameter of 7.99 bohr.

The lone band with -0.8 Rydberg energy at is due to the s-orbital of Oxygen. The fermi level energy is 0.46 Rydbergs with respect to the Muffin-Tin zero. The bands touching the fermi level are due to Oxygen's p-orbitals. At point their energy is 0.44 Rydbergs. The first nearest band higher than the fermi level has some s-orbital character and energy of 0.76 Rydbergs. The highest band above it has some d-orbital character.

These bands show that MgO is an insulator, as known experimentally.

The band gap energies at are listed and compared below:

Table 10 Band gaps of MgO at point.

	Band gap (s-p) eV	*Band gap (p-s) eV*
This work	16.87 (1.24 Ry)	4.35 (0.32 Ry)
Chang [Chang] et. al.	17.14	4.80
Fiermans [Fiermans] et. al. Experimental, as reported in [Chang]	21.0	5 – 6

The density of states (DOS) for MgO are presented below. The plot below shows the total DOS in red with Magnesium contributions shown in other colors.

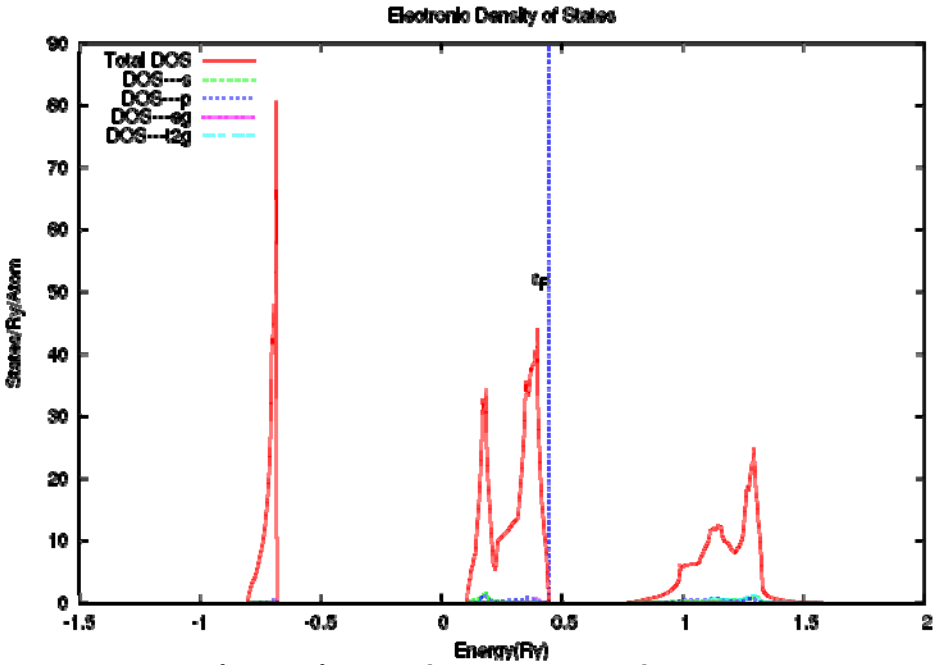

Figure 90: Density of States of MgO with Magnesium contributions.

The plot above shows that the Mg contribution to the density of states (DOS) is very small.

The plot below shows the total DOS in red with Oxygen contributions shown in other colors.

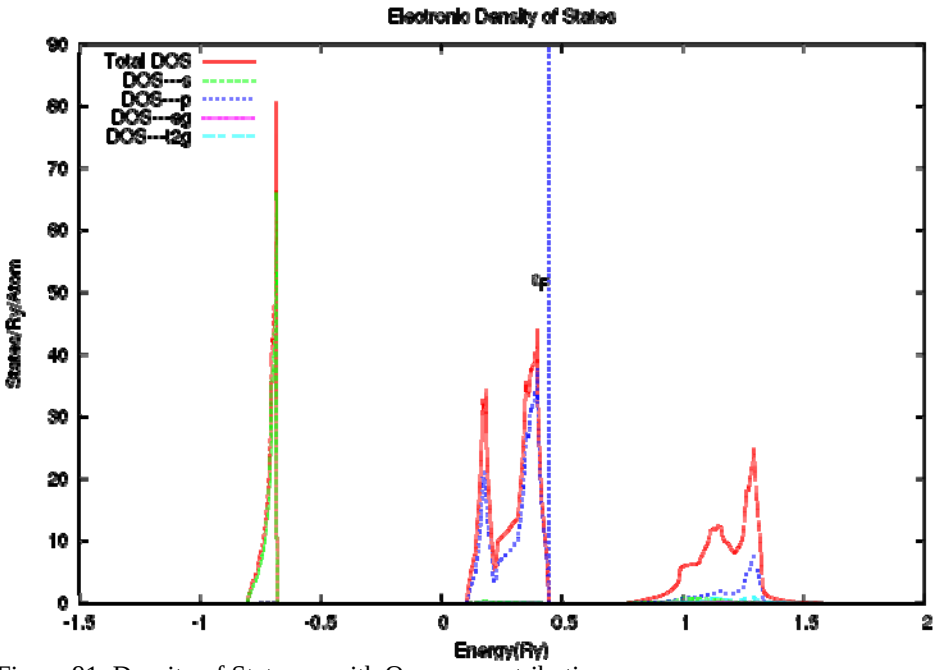

Figure 91: Density of States as with Oxygen contributions.

The low peak of the DOS has s-oxygen character and the DOS just below the fermi level has a p-oxygen character.

Chapter 11: Heavy Metals

MESP was used to perform APW computations on the following heavy metals:

Lawrencium (Lr), Atomic Number 103

Rutherfordium (Rf), Atomic Number 104

Dubnium (Db), Atomic Number 105

These metals do not exist freely and are synthesized by colliding lighter materials together to form these metals. They have very short half-lives: Lr 3.6 hours, Rf 1.3 hours, and Db 29 hours.

The findings of these computations are presented below.

Lawrencium

Electronic Configuration

The valence electrons of Lawrencium are estimated to be in the following electronic configuration:

5f14 6d1 7s2

Ground State

The following total energy plot shows the lowest energy curve for Lawrencium to be FCC and thus it is the ground state for the material.

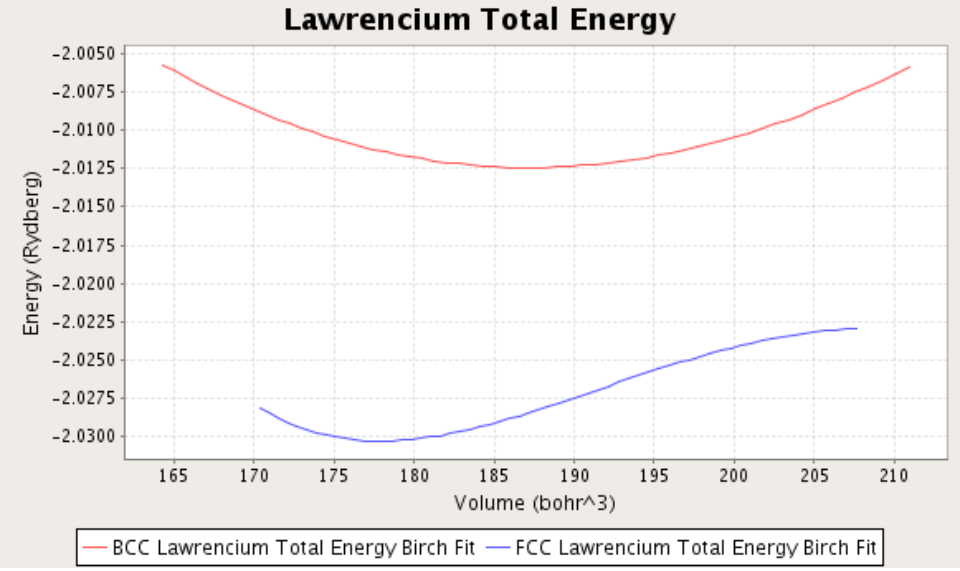

Figure 92: Total Energy vs. Volume

Lattice Parameter and Bulk Modulus

For FCC, the total energy as a function of the lattice parameter is depicted as:

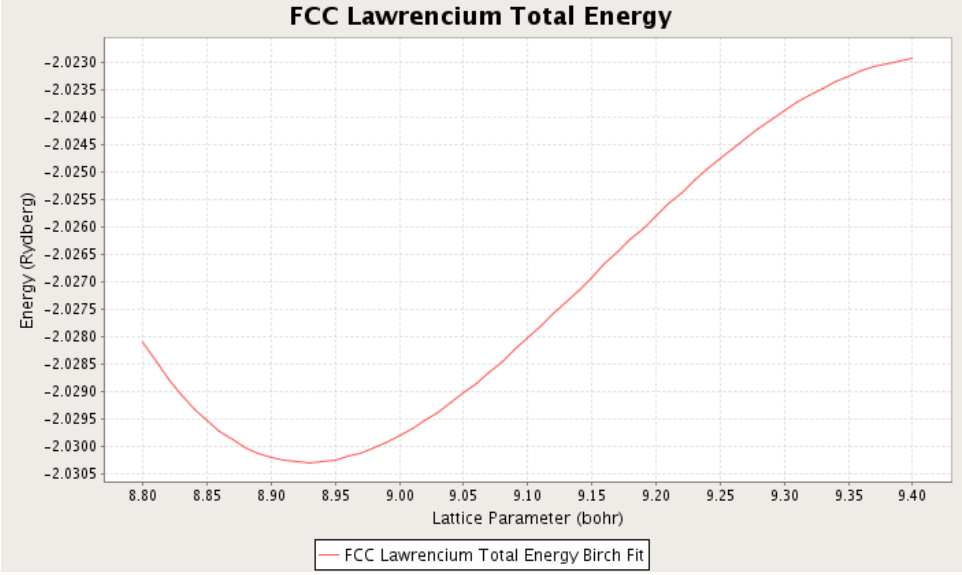

Figure 93: Total Energy vs. Lattice Parameter

The Birch-Murnaghan equation of order 3 determined the lattice parameter to be 8.928 bohr and Bulk Modulus to be 157.7 GPa.

Band Plot

The following plot shows the band energies at the equilibrium lattice parameter of FCC Lr.

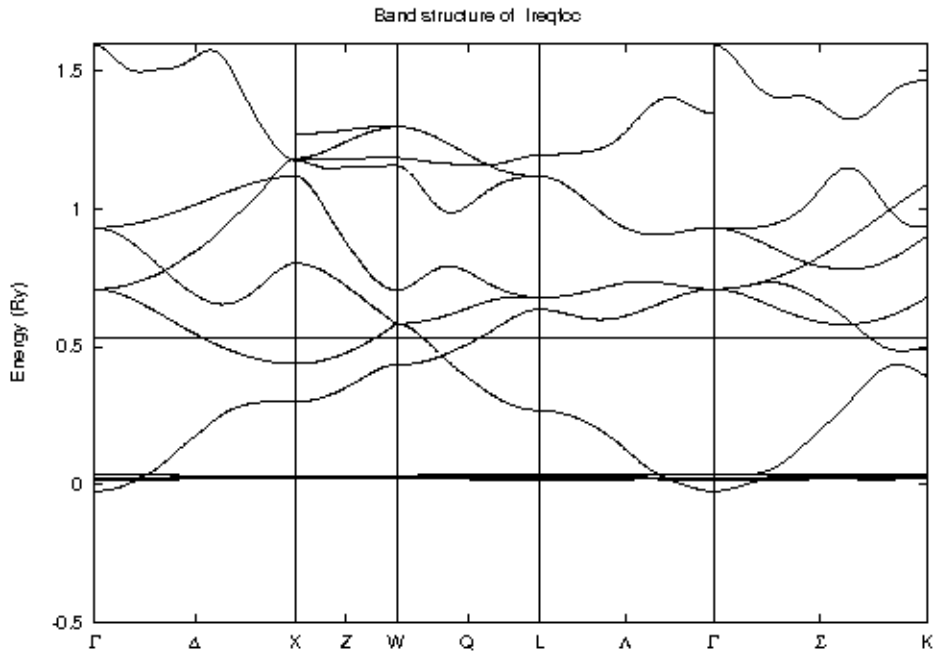

Figure 94: Band structure of Lr at equilibrium lattice parameter.

The bands crossing the fermi energy indicate that Lr is a metal. The thick and narrow bands near 0 Rydberg are due to the 5f orbitals. The band coming slightly lower than zero Rydberg and moving up is due to the 7s2 orbital. The rest are due to the 6d orbitals.

Density of States

The density of states for the ground state equilibrium lattice parameter is computed to be as below:

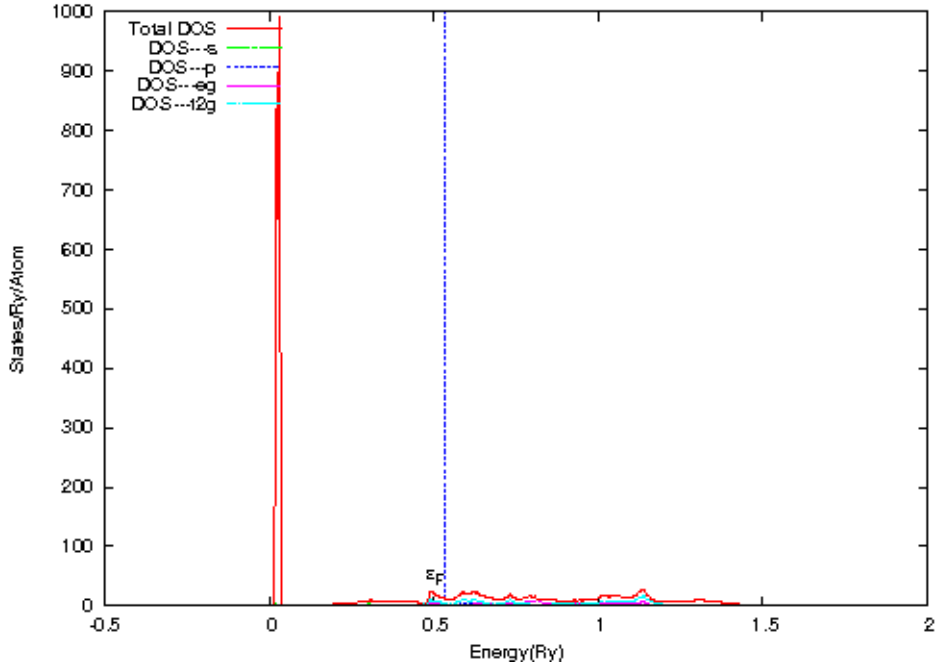

Figure 95: Density of states of Lr FCC.

The peak at about zero is f-dos.

A close-up of the higher energy states is presented below.

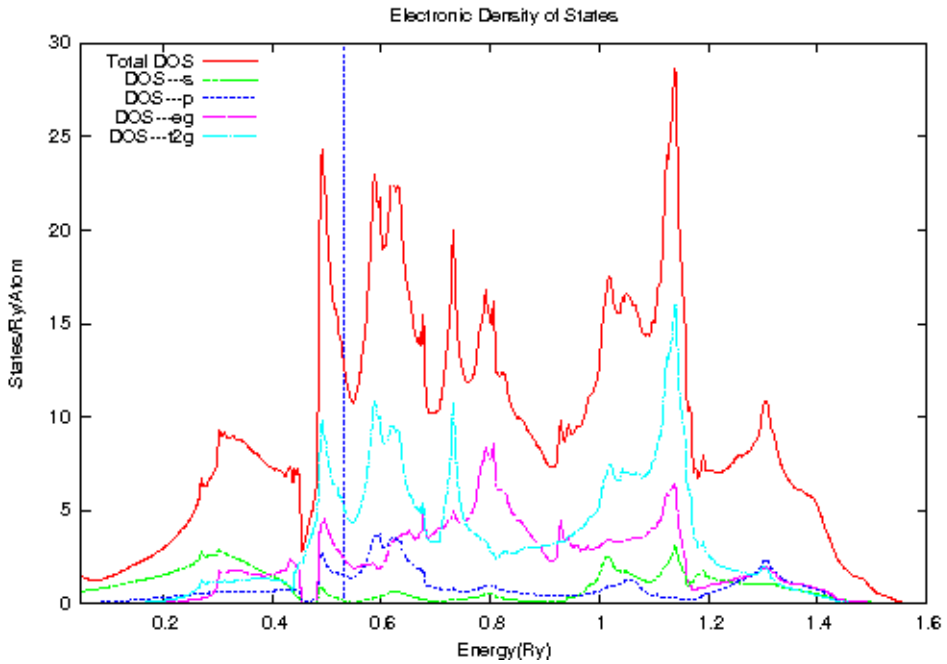

Figure 96: A close-up of the DOS towards the higher energy window shows the details of the DOS structure for FCC Lr.

The density of states at fermi level of 0.53 Rydberg, with respect to the Muffin-Tin zero, is as following:

Table 11 Density of States (DOS) decomposition of Lawrencium at fermi level

Orbital	*Density of States (states / Rydberg)*
s	0.18
p	1.51
d (eg)	2.43
d (t2g)	5.17
f	0.36
Interstitial	3.2
Total	12.85

The density of state at fermi level has substantial d orbital (specifically t2g) character. The fermi level value is given with respect to the muffin-tin zero (that is the constant potential outside the MT spheres).

Stoner Criterion of Ferromagnetism

I_F was computed to be 0.016 Ry. With total number of states at fermi level $N(E_F)$to be 12.85 / Ry, the Stoner criterion was determined to be 0.212, much less than the needed 1.0 for the metal to be ferromagnetic. Thus Lawrencium is expected not to be ferromagnetic.

Rutherfordium

Electronic Configuration

The valence electrons of Lawrencium are estimated to be in the following electronic configuration:

5f14 6d2 7s2

Ground State

The following total energy plot shows the lowest energy curve for Rutherfordium to be FCC and thus it is the ground state for the material.

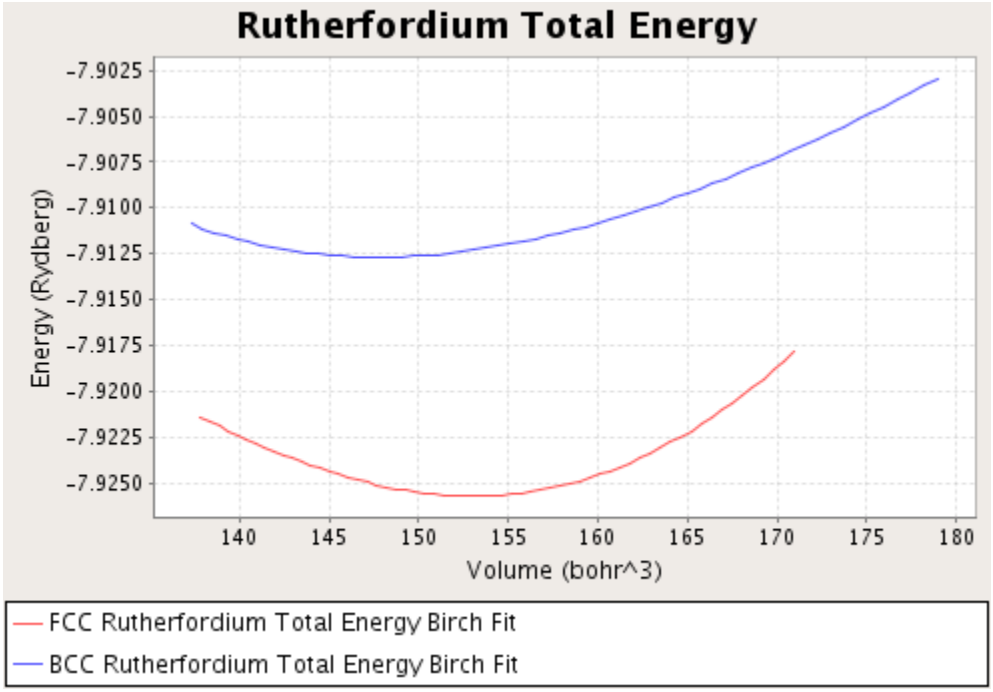

Figure 97: Total Energy vs. Volume

Lattice Parameter and Bulk Modulus

For FCC, the total energy as a function of the lattice parameter is depicted as:

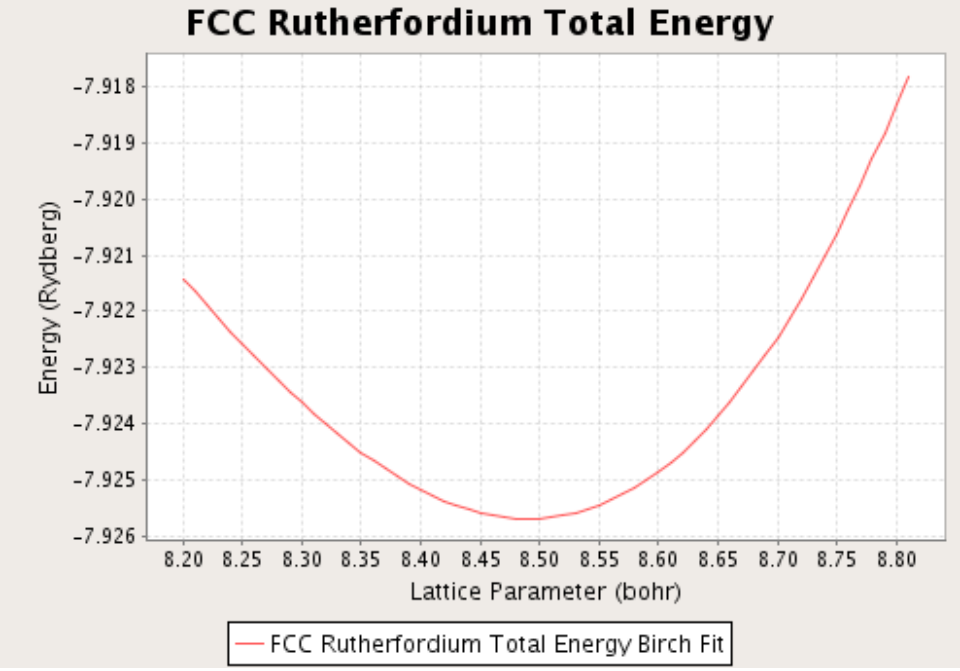

Figure 98: Total Energy vs. Lattice Parameter

The Birch-Murnaghan equation of order 3 determined the lattice parameter to be 8.49 bohr and Bulk Modulus to be 102.0 GPa.

Band Plot

The following plot shows the band energies at the equilibrium lattice parameter of FCC Rf.

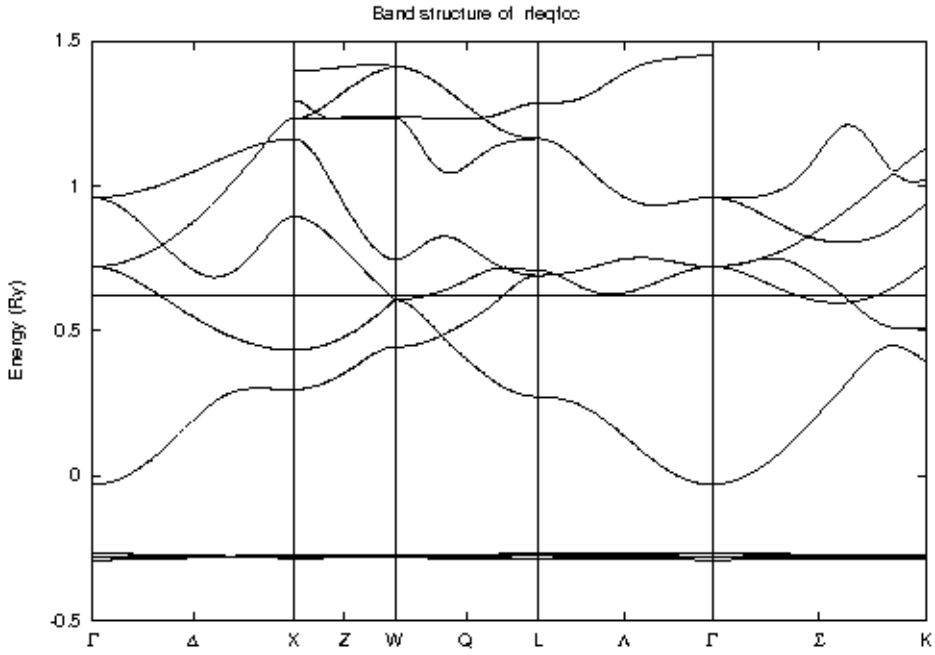

Figure 99: Band structure of Rf at FCC equilibrium lattice parameter.

The bands crossing the fermi energy indicate that Rf is a conductor. The thick and narrow bands near 0.27 Rydberg are due to the 5f orbitals. The band coming slightly lower than zero Rydberg and moving up is due to the 7s2 orbital. The rest are due to the 6d orbitals.

Density of States

The density of states for the ground state equilibrium lattice parameter is computed to be as below:

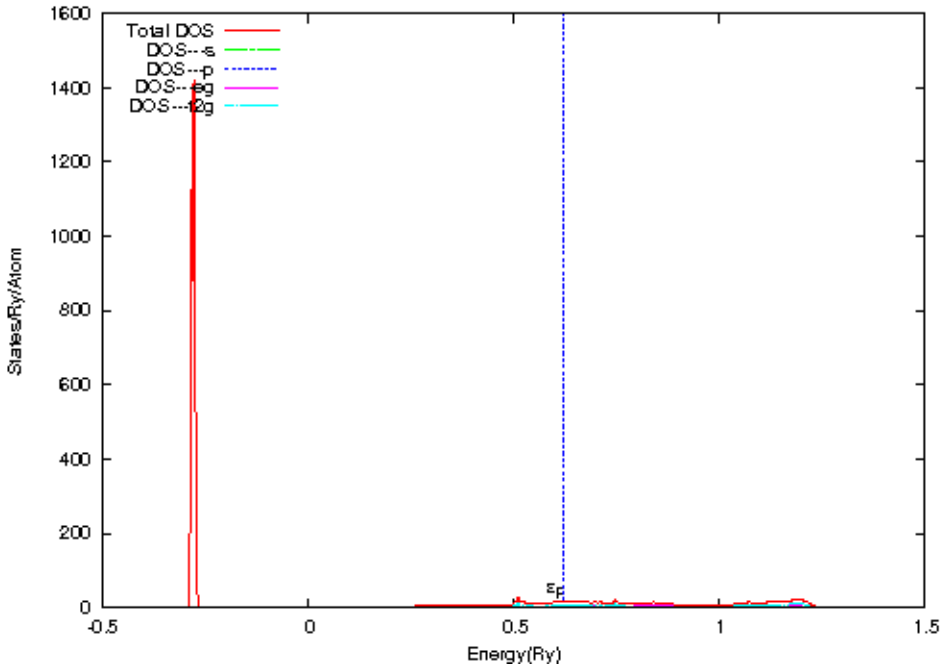

Figure 100: Density of states of Rf at FCC equilibrium parameter.

The peak at about zero is the f-dos.

A close-up of the higher energy states is presented below:

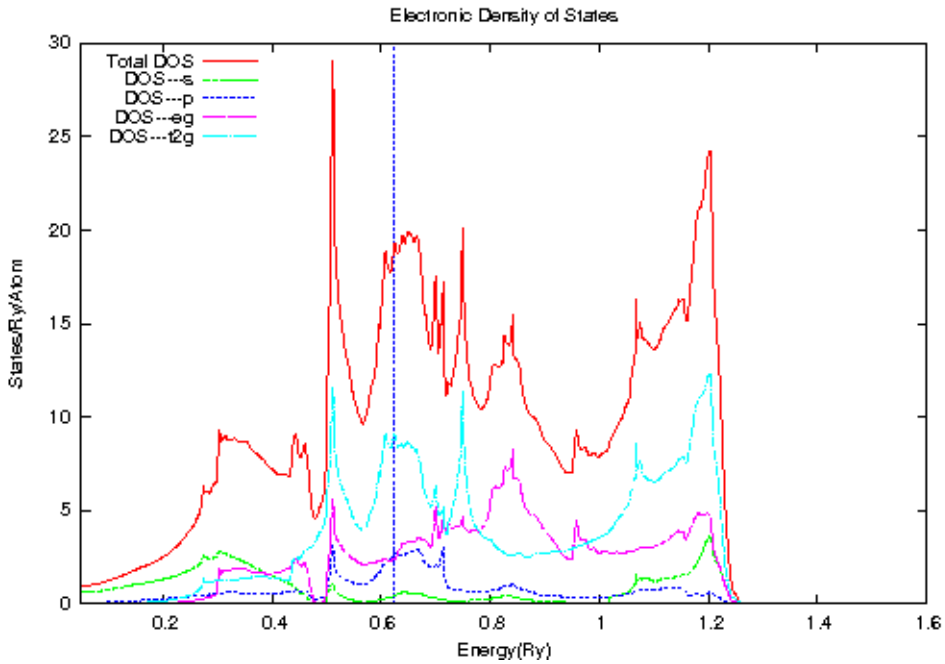

Figure 101: Higher energy density of states of FCC Rf.

The density of states at fermi level of 0.62 Rydberg, with respect to the Muffin-Tin zero, is as following:

Table 12 Density of States (DOS) decomposition of Rutherfordium at fermi level

Orbital	*Density of States (states / Rydberg)*
s	0.41
p	2.61
d (eg)	2.41
d (t2g)	8.80
f	0.57
Interstitial	4.06
Total	18.86

The density of state at fermi level has substantial d orbital (specifically t2g) character. The fermi level value is given with respect to the muffin-tin zero (that is the constant potential outside the MT spheres).

Stoner Criterion of Ferromagnetism

I_F was computed to be 0.016 Ry. With total number of states at fermi level $N(E_F)$to be 18.8 / Ry, the Stoner criterion was determined to be 0.308, much less than the needed 1.0 for the metal to be ferromagnetic. Thus Rutherfordium is expected not to be ferromagnetic.

Dubnium

Electronic Configuration

The valence electrons of Lawrencium are estimated to be in the following electronic configuration:

5f14 6d3 7s2

Ground State

The following total energy plot shows the lowest energy curve for Dubnium to be BCC and thus it is the ground state for the material.

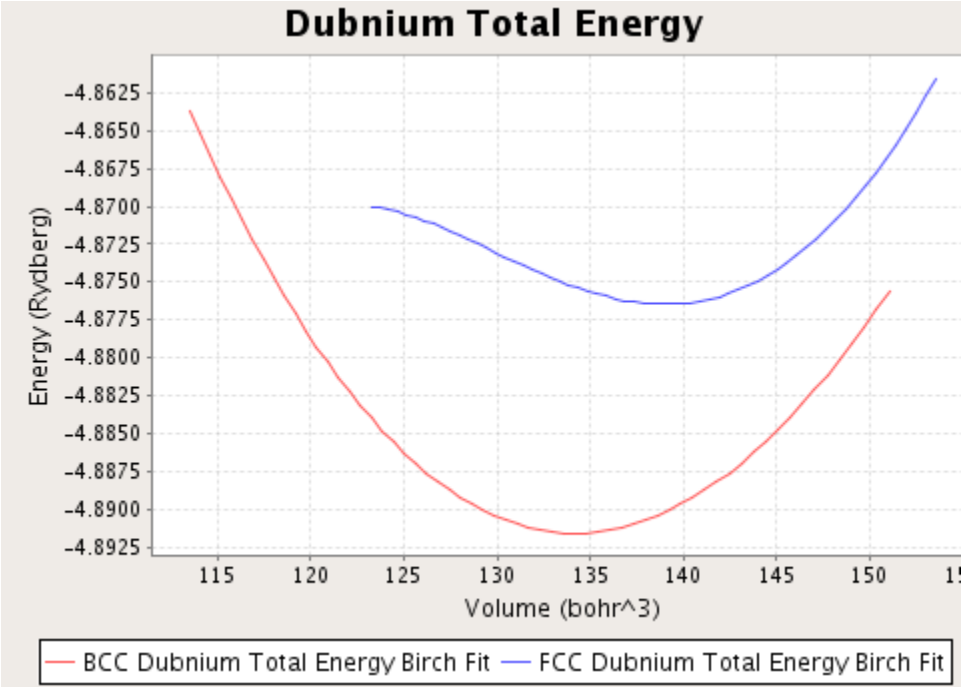

Figure 102: Total Energy vs. Volume

Lattice Parameter and Bulk Modulus

For BCC, the total energy as a function of the lattice parameter is depicted as:

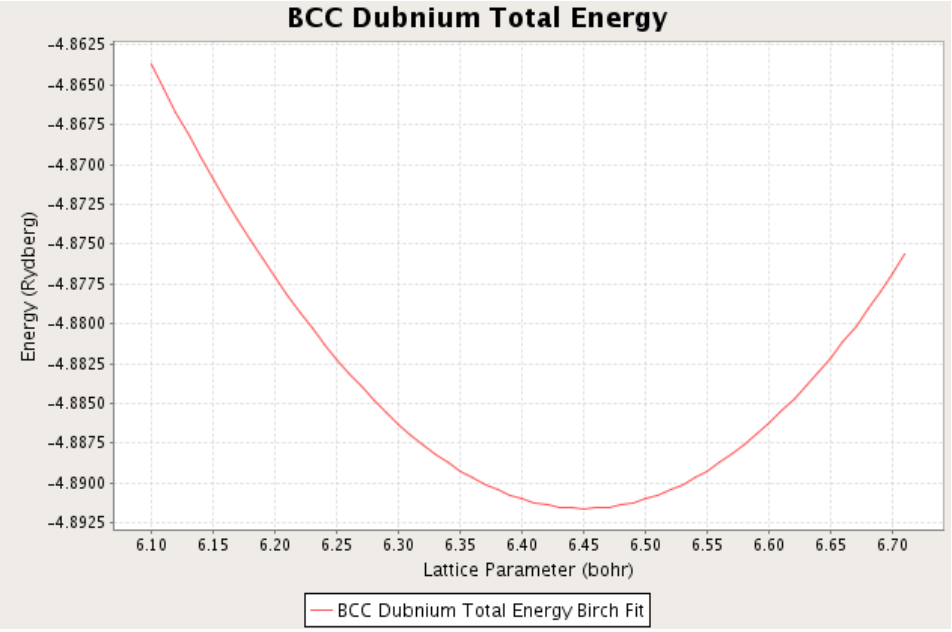

Figure 103: Total Energy vs. Lattice Parameter

The Birch-Murnaghan equation of order 3 determined the lattice parameter to be 6.45 bohr and Bulk Modulus to be 240.22 GPa.

Band Plot

The following plot shows the band energies at the equilibrium lattice parameter of FCC Db.

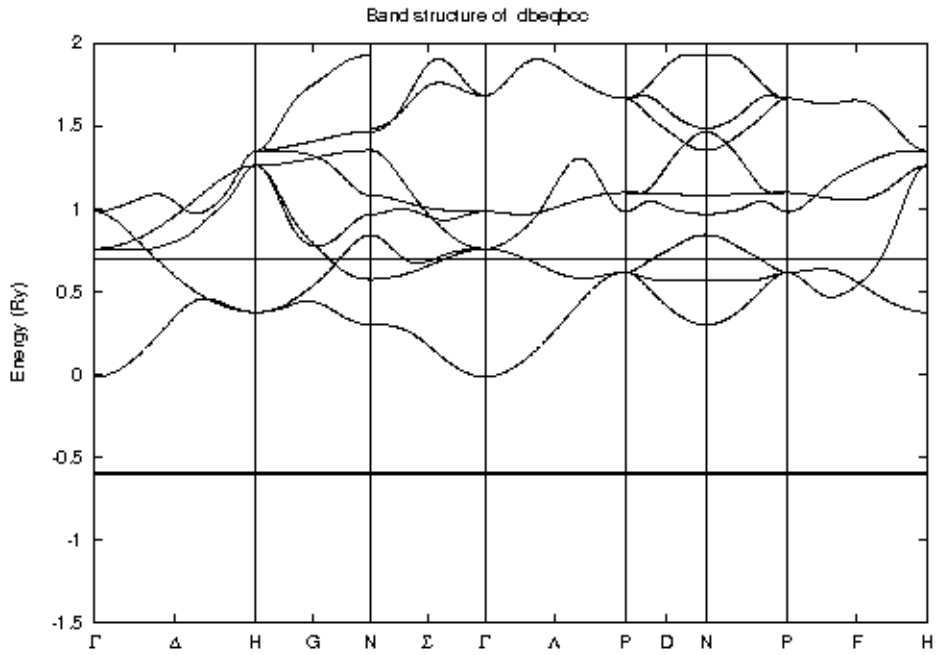

Figure 104: Band structure of Db at BCC equilibrium lattice parameter.

The bands crossing the fermi energy indicate that Db is a conductor. The thick and narrow bands near -0.6 Rydberg are due to the 5f orbitals. The band coming slightly lower than zero Rydberg and moving up is due to the 7s2 orbital. The rest are due to the 6d orbitals.

Density of States

The density of states for the ground state equilibrium lattice parameter is computed to be as below:

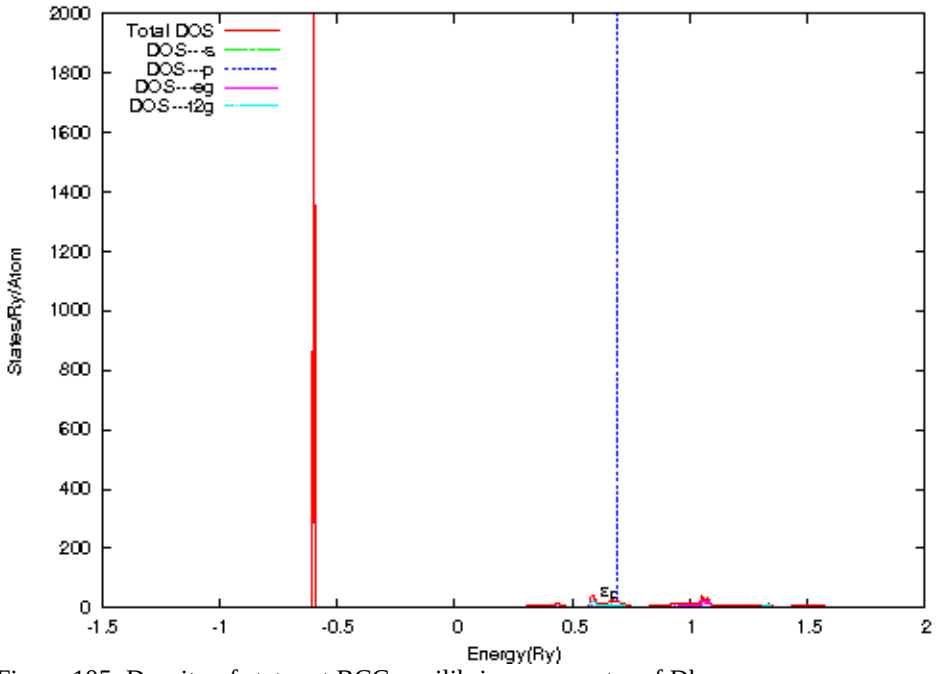

Figure 105: Density of states at BCC equilibrium parameter of Db.

The peak at about zero is the f-dos.

A close-up of the higher energies reveals:

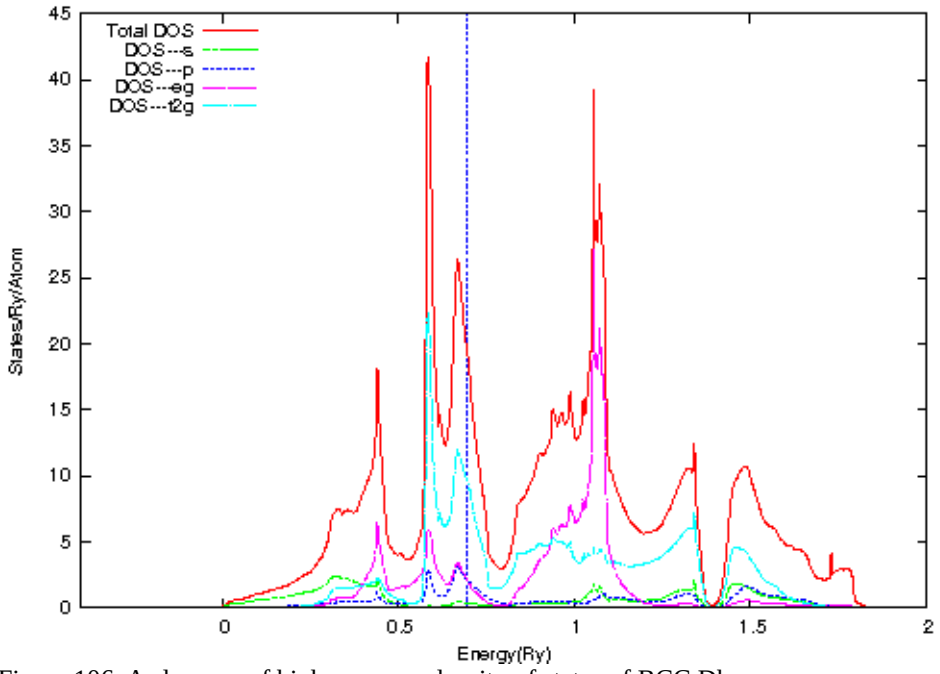

Figure 106: A close-up of higher energy density of states of BCC Db.

The density of states at fermi level of 0.69 Rydberg, with respect to the Muffin-Tin zero, is as following:

Table 13 Density of States (DOS) decomposition of Dubnium at fermi level

Orbital	*Density of States (states / Rydberg)*
s	0.33
p	2.14
d (eg)	2.19
d (t2g)	9.72
f	0.45
Interstitial	4.82
Total	19.65

The density of state at fermi level has substantial d orbital (specifically t2g) character. The fermi level value is given with respect to the muffin-tin zero (that is the constant potential outside the MT spheres).

Stoner Criterion of Ferromagnetism

I_F was computed to be 0.014 Ry. With total number of states at fermi level $N(E_F)$ to be 19.65 / Ry, the Stoner criterion was determined to be 0.289, much less than the needed 1.0 for the metal to be ferromagnetic. Thus Dubnium is expected not to be ferromagnetic.

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Curriculum Vitae

Mir Mohammed Assadullah graduated from Adamjee Government Science College, Karachi, Pakistan in 1982. He received his BA from Ohio Wesleyan University in 1987, majoring in Computing Science and Mathematics. His minor was Economics. There he was elected into the national mathematics honorary society of Pi Mu Epsilon. He received his MS from the Courant Institute of Mathematical Sciences of New York University in Computer Science during 1989. Thereafter he worked in Information Technology industry and helped start several dot com companies, as well as served in large organizations. He is also a certified Project Management Professional.

He joined the Computational Sciences and Informatics PhD program in 2005 and received his PhD in 2010 in the same program.