EXPANSION OF THE NRL TIGHT-BINDING METHOD TO INCLUDE F-ORBITALS AND APPLICATION IN THORIUM AND ACTINIUM

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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Dedication

I dedicate this work to my family.
Acknowledgments

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Abstract

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The current NRL Tight-Binding suite of programs was designed to only include s, p, and d orbitals in the basis. Because of this limitation, materials which have significant f orbital interactions could not be modeled in the current program. My dissertation expanded the NRL Tight Binding program to account for f orbital interactions and then used the modified program to investigate Thorium and Actinium, materials whose properties are influenced by the f electrons. Using the improved program, I was able to develop a set of Slater-Koster polynomial coefficients for both Thorium and Actinium which accurately reflected experimental properties such as total energy (fcc, bcc, sc, hcp, and diamond), energy bands, density of states, elastic constants, and phonon frequencies.
Chapter 1: Introduction

The objective of this dissertation is to advance the understanding of how to best model materials whose properties depend on f orbitals so that accurate estimates of their physical properties under varying conditions, such as pressure and temperature, can be predicted. The physical interaction of the f orbitals in extended families of materials has a great impact on their chemical properties. Recent research indicates that rare earth elements (e.g. lanthanides and actinides Figure 1.1) could have significant application in magnets, superconductive devices, batteries, and computers and that those properties may be due to the interaction of the f orbitals in these materials. Contrary to their name, rare earth elements are not particularly rare, but are normally found in low concentrations. Because it is expensive to extract sufficient quantities of these materials, they are less used than some other more readily available materials and the need for accurate computer-based ways to predict their material properties is of crucial importance. There have been several investigations of the band structure and total energy of these materials using first-principles methods based on density functional theory. However, currently no investigation has produced a complete set of transferable tight-binding parameters to model the behavior of these materials. To get this complete picture of the materials, the software of the Naval Research Lab Tight Binding program (NRL-TB) will be extended to include the effects of f-orbitals and the expanded program codes will be used to investigate Thorium and Actinium.

The process for solving the Schrödinger equation in a periodic lattice was first described by Bloch. By introducing a linear combination of atomic orbitals (LCAO), the Schrödinger equation can be transformed into a solvable system of algebraic equations.[1] However, a complication is introduced by the general Bloch solution process; many complex integrals need to be evaluated to solve the system of equations. One simplification of the Bloch process which can be done is to use orthogonal orbitals.[2] This modification eliminates
many of the interacting integrals; however, even this lesser number of integrals can make the problem too difficult to solve for a large system. Slater and Koster introduced the innovative idea of replacing the integrals with disposable parameters. [3] The investigator fits locations of high-symmetry within the Brillouin zone to first-principles computations to determine the best set of parameters for a material. In the original paper by Slater and Koster, only s, p, and d orbitals were considered. In 1974, Lendi expanded the Slater-Koster process to include f-orbitals. [4] A set of general expressions for reducing the LCAO integrals to two-center approximations was later published by Sharma in 1979. [5] Finally, in 2004, Podolskiy and Vogl published a compact Hamiltonian matrix formulation to compute the Slater-Koster parameter expressions for the Bloch integrals. [6] The use of this compact Hamiltonian matrix formulation allows expansion to higher orbitals if necessary and avoids much of the danger in miscoding the integrals.

This dissertation focuses on applying the Podolskiy and Vogl approach to build an extension of the NRL Tight-Binding Method to include f-orbitals. [7][8] Previous work
along this line has been done by Jones and Albers based on the NRL Tight-Binding code applied to Uranium (U). [9] In a more recent paper, Jones and Albers built on the earlier research to include spin-orbit coupling and applied the modified approach to investigate the density of states (DOS) and band structure for Th, U, and Pu. [10] However, these authors did not succeed in having simultaneously fit the bands and the total energies and having adequate transferability of their parameters to other structures as we have achieved in the present work. Our investigation differs from those previous works in two significant ways. First, the implementation of the expansion for the NRL Tight-Binding program will be done using the compact Hamiltonian matrix formulation developed by Podolskiy and Vogl with the singularity correction explained by Hourahine. [6] [11] Second, a complete set of material properties will be examined once the best fit set of polynomial coefficients is determined. Following chapters in this dissertation will explain the process I adopted for the code expansion, insights and potential improvements to the fitting process, and a summary of the best fit material properties for Thorium and Actinium.

This dissertation manuscript is composed of five parts. Chapter 2 presents a broad overview of the theories and methods which are associated with this investigation. Chapter 3 gives a more detailed description of the progression of the history and mathematics associated with tight-binding theory and the specifics of how the NRL-TB program had to be modified. Chapter 4 explains how the improved program was used to investigate Thorium and compares the results to the associated LAPW calculations. Chapter 5 explains how the improved program was used to investigate Actinium and compares the results to the associated LAPW calculations. Chapter 6 describes changes which could be made to other related programs (e.g. the NRL Molecular Dynamics model) and other avenues for analysis that could be done.
Chapter 2: Theory and Methods

2.1 Introduction

This chapter provides an overview of the calculations and methods associated with electronic structure calculations. The central problem which is being addressed in all cases is how to approach solving the time independent Schrödinger equation. These first-principles, or ab initio, calculations try to make as few approximations as possible, but as the number of atoms being examined increases, the difficulty in computing true first-principles results reaches the limits of computational power. Density Functional Theory (DFT) proves that there is a direct relationship between the total energy, $E$, of a system and its ground state electronic density, $\eta$. Furthermore, Hohenberg and Kohn (1964) showed that the ground state electronic density is the density that minimizes $E(\eta)$. The theory of DFT is then made practical by expressing the total energy of a system as a sum of energies which can be accurately computed and a final exchange correlation energy, $E_{xc}$, which accounts for the energy due to the many body particle interactions and must be approximated. Two popular methods for calculating $E_{xc}$ are the Local Density Approximation (LDA) and the Generalized Gradient Approximation (GGA). Kohn and Sham (1965) showed that there is a relationship between $E_{xc}$ and a density dependent potential $V_{xc}$ which allowed for the development of an iterative process for solving for the ground state electronic density. In the process one estimates an initial density, $\eta_i$, to allow for the solution of a potential, $V_i$, which is then used to solve the Kohn-Sham equations for the eigenstates which in turn allows the computation of a possibly different density, $\eta_j$. The true minimum ground state electronic density is found when $\eta_i$ and $\eta_j$ are self-consistent. The solutions from DFT combined with Tight-Binding Methods can then be used to examine all the properties within a crystal. In the Tight-Binding methodology introduced by Slater and Koster, solutions to
the Schrödinger equation at certain locations of high symmetry within the crystal lattice are used to determine a set of fitting parameters which can then be used to find other energy values in the crystal through interpolation.[3]

2.2 Density Functional Theory

The basic scientific theory used to study the electronic structure and total energy of any system of atoms and electrons is Density Functional Theory (DFT).[12] The Hohenberg-Kohn theorem demonstrated the existence of a one-to-one mapping between the ground state electron density and the ground state wavefunction of the many-body system. Given that a ground state electron density can be found, all properties of a system associated with the ground state electron density can then be calculated.[13]

The functional for the energy is defined as

$$E(\eta) = T(\eta) + E_{e-e}(\eta) + E_{e-n}(\eta) + E_{n-n}(\eta) + E_{xc}(\eta)$$

(2.1)

where $T(\eta)$ represents the independent particle kinetic energy, $E_{e-e}(\eta)$ are the electron to electron interactions, $E_{e-n}(\eta)$ are the electron to nuclei interactions, $E_{n-n}(\eta)$ represent the interaction of the nuclei, and $E_{xc}(\eta)$ contains all the many body effects of exchange and correlation. Kohn and Sham defined the electron density as a sum of single particle densities and then used the variational principle to determine the minimum for that set of electronic densities. This method replaces the many-body electronic wavefunction with a set of single particle Schrödinger-like equations

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

(2.2)
with the charge density $\eta$ equal to the sum of the squares of the atomic wavefunctions

$$\eta = \sum_{i} \psi_{i}^{*} \psi_{i}$$  \hspace{1cm} (2.3)$$

Similar to the DFT formulation, the potential, $V(r)$, is replaced with the expression

$$V(r) = V_{c}(r) + V_{xc}(r)$$  \hspace{1cm} (2.4)$$

where $V_{c}(r)$ is the Coulomb potential and $V_{xc}(r)$ is the unknown exchange and correlation potential encompassing the many particle potential interactions. Both $V_{c}(r)$ and $V_{xc}(r)$ are related to the charge density, $\eta$. $V_{c}(r)$ is solved for via Poisson’s equation

$$\nabla^{2}(V_{c}(r)) = -8\pi \eta(r)$$  \hspace{1cm} (2.5)$$

and $V_{xc}(r)$ is related to the original exchange and correlation energy, $E_{xc}(\eta)$

$$V_{xc}(r) = \frac{\partial E_{xc}(\eta)}{\partial \eta}$$  \hspace{1cm} (2.6)$$

Substituting equation 2.4 into equation 2.2 yields the set of equation known as the Kohn-Sham equations

$$\left[ -\frac{\hbar^{2}}{2m} \nabla^{2} + V_{c}(r) + V_{xc}(r) \right] \psi_{i}(r) = \epsilon_{i} \psi_{i}(r)$$  \hspace{1cm} (2.7)$$

and because of the coupling of $V_{xc}(r)$ and $E_{xc}(\eta)$, the Kohn-Sham equations need to be solved in an iterative fashion which produces as self-consistent solution.
2.3 Self-Consistent Cycle

In the KS system, the charge density is related to the exchange and correlation energy $E_{xc}$ is related to both the input through the exchange and correlation potential, $V_{xc}$, and to the output in the total energy.\[12\] Because of this, we solve the KS equations in an iterative fashion which seeks to find a charge density which produces an effective potential which when substituted into the Kohn-Sham equations reproduces the original charge density. This self-consistency loop is shown in Figure 2.1.\[12\] In this process, we start with an estimated charge density, $\eta_i$, which allows the calculation of the initial potential, $V_i$ via equation 2.4. Then, using $V_i$ the Kohn-Sham (KS) equations are solved to determine the eigenstates. The eigenstates are then used to calculate a charge density by summing over the occupied states in the solution, $\eta_j = \sum_j \psi_j^* \psi_j$. If the two results, $\eta_i$ and $\eta_j$, are within an acceptable tolerance than the solution has converged and no new iterations are needed. If the solution has not converged, then the original $\eta_i$ and $\eta_j$ are mixed and the resulting new estimate for the potential is used to continue the process.

Since a universal function for $E_{xc}$ is not known and it must be approximated. Two

![Figure 2.1: Self-Consistency Loop](image)
common methods for approximating the $E_{xc}$ term are the Local Density Approximation (LDA) and the Generalized Gradient Approximation (GGA).

### 2.4 Local Density Approximation

In the case of the Local Density approximation, the $E_{xc}$ is approximated by

$$E_{xc}(\eta) = \int d^3r \eta(r) \varepsilon_{xc}(\eta(r)) \quad (2.8)$$

where the $\varepsilon_{xc}(\eta(r))$ is approximated by a local function of the density which produces the same energy as a uniform electron gas.[12] The associated exchange correlation potential, $V_{xc}$ associated with the LDA is

$$V_{xc} = \frac{\partial E_{xc}(\eta)}{\partial \eta} = \varepsilon_{xc}(\eta) + \eta \frac{\partial \varepsilon(\eta)}{\partial \eta} \quad (2.9)$$

In the case of a homogeneous electron gas, $\eta$ is known analytically and the $V_{xc}$ can be computed dependent on how one chooses to model the governing the interaction of the gas, $\varepsilon_{xc}(\eta(r))$.

Though there are many forms of $V_{xc}$, only small variations in the computed results tend to be seen. Two examples of $V_{xc}$ are the $X_\alpha$ method[15][16] and the Hedin-Lundqvist form[17]. The $X_\alpha$ method expresses the exchange and correlation energy as

$$V_{xc}(r) = \alpha \left( \frac{3\eta(r) \frac{r}{8\pi}}{2} \right) = \alpha U_{ex}(r) \quad (2.10)$$

where the coefficient $\alpha$ is varied normally between $\frac{2}{3}$ and 1 to match the calculated energy
\( U_{\text{ex}}(r) \) for the atom. In the Hedin-Lundqvist form \( V_{xc} \) is expressed as[17]

\[
V_{xc}(r) = \alpha \beta(r_s) U_{\text{ex}}(r)
\] (2.11)

where \( \alpha = \frac{2}{3} \) and \( \beta \) is an enhancement factor defined by

\[
\beta(r_s) = 1 + B \ln \left( 1 + \frac{1}{x} \right)
\] (2.12)

using \( r_s = \left( \frac{3}{4\pi\eta(r)} \right), \ x = r_s/21, \) and \( B = 0.7734 \)

### 2.5 Generalized Gradient Approximation

The Generalized Gradient Approximation (GGA) differs from the LDA because the GGA includes information about the derivatives of the electronic density in the calculation of the \( E_{xc} \).[18] The general form of the GGA \( E_{xc} \) is

\[
E_{xc}^{GGA}(\eta) = \int \eta(r) \varepsilon_{xc}^{GGA}(\eta(r), \nabla \eta(r)) \, dr
\] (2.13)

where \( \eta(r) \) is the electron density and \( \varepsilon_{xc}^{GGA} \) represents an exchange and correlation interaction which is responsive to the gradient of the electron density. The GGA improves the agreement with experiment in the equilibrium lattice parameters for the alkali and alkaline earth metals while it does not improve the results in the transition metals. In the present work, we find that the GGA results agree better with experiment for Th while for Ac the opposite is true.
2.6 Born-Oppenheimer Approximation

An approximation to the original DFT calculations which can be made is to discount certain interactions which are known to contribute little to the overall energy. In the Born-Oppenheimer Approximation, we seek to separate the motion of the electrons and the nucleus. The DFT calculations are done at \( T = 0 \text{K} \), then the nuclei of the atom can be “frozen”. Since the nuclei are “frozen” and greatly outweigh the electrons, the energy associated with the motion of the nuclei can be ignored.

2.7 Electronic Structure Methods

Electronic structure methods seek to solve the Schrödinger equation by expanding the original wavefunction, \( \psi(r) \) into a sum of wavefunctions, \( \phi_i(r) \)

\[
\psi(r) = \sum_i a_i \phi_i(r)
\]

This changes the original many-body Schrödinger equation into a system of linear algebraic equations. By minimizing the system, the appropriate set of \( a_i \)’s can be found which describes the original wavefunction. Many methods have been developed to solve these systems of equations with their primary differences being in what simplifications are made in considering the core electrons and what form of the wavefunctions are chosen to describe the \( \phi \)’s. All electron methods consider the impact of all of the electrons in the core during the solution process. Both the Augmented Plane Wave and Linearized-Augment Plane Wave methods are all electron methods. Pseudopotential methods “freeze” the core electrons and solve the Schrödinger equation only for the valence electrons. In these cases the complex effects associated with the core electrons is replaced with an alternate or “pseudo” potential; this pseudopotential replaces the normal Coulomb core potential contribution. Since our research used results from LAPW methods, a little more detail about the APW and LAPW methods will be provided.
2.8 Augmented Plane Wave (APW) Method

One of the most successful methods to compute the electronic structure of a material using DFT and the Kohn Sham approach is through the Augmented Plane Wave (APW) method. This first-principles method is designed to solve the Schrödinger equation for a periodic solid.[19] The wavefunction in the DFT is expanded in terms of basis functions which depend upon the distance from the nuclei. Inside the spheres, the potential and wavefunction vary spherically; however, between the atoms the potential and wavefunction remain constant. So, within some defined distant of the atom, the potential, \( V(r) \), is spherically symmetric, \( V(|r - R_n|) \) and the associated wavefunctions are describe by spherical harmonics, \( Y_{lm} \),

\[
\phi (r) = \sum_{lm} A_{lm} Y_{lm} (r) u_l (r, \varepsilon) \quad (2.15)
\]

For the interstitial region, the potential is a constant, \( V_c \) and the associated wavefunction takes the form of a plane wave

\[
\phi_i (r) = e^{ikr} \quad (2.16)
\]

A schematic of the potential is shown in Figure 2.2. This approximation of the potential is more commonly known as the Muffin Tin approximation because of its resemblance to a muffin tin. The \( A_{lm} \)'s are determined by enforcing the continuity of the wavefunction at the boundary between the inner and outer regions. The \( u_l \)'s are computed by solving the radial equation at each k-point in the Brillouin zone[12]

\[
\left[-\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + V(r) - \varepsilon_i \right] ru_l (r) = 0 \quad (2.17)
\]

Since the described potential \( V(r) \) is periodic, the wavefunction satisfies the Bloch condition

\[
\Psi (r + G_n, k) = e^{ikG_n} \Psi (r, k) \quad (2.18)
\]
By substituting equation 2.18 into equation 2.14 as set of \( N \) algebraic equations are produced

\[
\sum_{j=1}^{N} (H - \varepsilon_i) a_j = 0 
\]  
(2.19)

Legendre polynomials, spherical Bessel functions, and logarithmic derivatives of \( u_i' / u_i \) must be calculated when filling in the APW matrix.

### 2.9 Linearized Augmented Plane Wave (LAPW) Method

The LAPW method seeks to improve upon the APW method by matching the basis functions and their derivatives to a radial wavefunction at \( \varepsilon_i \). This is known as linearization of the APW functions which solves problems in the diagonalization of the APW secular equations and facilitates the implementation of a general potential. The radial equation 2.17
from the APW method becomes \[ [−\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + V(r) − \varepsilon_i] ru_l(r) = ru_l(r) \] (2.20)

for the LAPW method where the \( u_l \) are defined at fixed \( \varepsilon_l \). In the specific implementation of the LAPW method used to produce our input database, several additional changes have been made which separate it from the APW Method described earlier. First, the Muffin-Tin approximation is removed and a general potential is used (i.e. the potential inside the spheres is not restricted to be spherically symmetric and outside the spheres is not restricted to be a constant). Second, the GGA is also integrated into the code which can provide more accurate results in certain cases.

\section*{2.10 Tight-Binding Calculations}

Another approach is to solve the Schrödinger equation via a Linear Combination of Atomic Orbitals (LCAO) or Tight-Binding (TB) method. These methods have the advantage of being fast because the matrix to be diagonalized is small. In this method the atomic orbitals are replaced by Bloch sums

\[ \sum e^{ik \cdot R} \phi_n(r - R_i) \] (2.21)

Further, the \( \phi \)'s in the above equation can be replaced by an orthogonalized basis such that each Hamiltonian matrix element is defined by

\[ H_{\alpha \beta} (k) = \sum e^{ik \cdot R} \int \phi_{\alpha}^* (r - R_\alpha - b_i) H \phi_{\beta} (r - b_i) \, d^3r \] (2.22)

With the above description of the Hamiltonian, there are potentially four different kinds of integrals depending on the locations of the interacting particles and the location of the potential

1. On-site integrals : all three locations in the same atom
2. Two-center integral: one wavefunction co-located with the potential

3. Three-center integral: both wavefunctions and potential are not co-located

4. Crystal field integral: potential in a separate location but wavefunctions co-located.

In many implementations of the Tight-Binding method, the first two of these integrals are used and the others neglected. With this simplification, the integrals will only depend upon the displacement of the particles. The Slater-Koster Tight Binding method bypasses solving these integrals, and instead treats them as disposable parameters. These parameters are determined by fitting a set of first-principles results, usually at points and directions of high symmetry in the Brillouin zone. Once the best parameters are found, the eigenvalues in the entire Brillouin zone can be determined through interpolation.

2.11 Total Energy

The DFT calculations provide the total energy, \( E(V) \) as a function of volume. Examining the total energy at various lattice constants, a determination of the equilibrium lattice constant can be made. The standard for examining the total energy is through the Birch fit formulation[20]

\[
E(V) = \sum_{i} a_i V_i^{-2/3}
\]

where \( a_i \) are expansion coefficients and \( N \) is the order of the fit. Since the lattice energy tends to vary in a parabolic fashion, expanding the Birch fit up to \( N = 3 \) is usually sufficient. Expanding 2.23 to \( N = 3 \) yields

\[
E = E_0 + \frac{9}{8} B_0 V_0 \left[ \left( \frac{V_0}{V} \right)^{2/3} - 1 \right]^2 + \frac{9}{16} B_0 V_0 \left( B_0' - 4 \right) \left[ \left( \frac{V_0}{V} \right)^{2/3} - 1 \right]^3 + \sum_{n=4}^{N} \gamma_n \left( \left( \frac{V_0}{V} \right)^{2/3} - 1 \right)^n
\]

(2.24)
$E_0$ is the equilibrium energy, $V_0$ is the equilibrium volume, $B_0$ is the equilibrium bulk modulus, and $B_0'$ is the pressure derivative of the equilibrium bulk modulus. Hence, via the Birch fit, we determine both the equilibrium lattice constant and the bulk modulus.

### 2.12 Elastic Constants

This section provides a brief description of the equations associated with computing the elastic constants for systems with cubic symmetry.[21] For a given strain matrix, \{\epsilon_i\}, the total energy changes from its equilibrium value, $E_0$ to

$$E(\epsilon_i) = E_0 - P(V) \Delta V + \frac{V}{2} \sum_{ij} C_{ij} \epsilon_i \epsilon_j + O[\epsilon_i^3]$$ (2.25)

where $V$ is the volume of the undistorted lattice, $P(V)$ is the pressure of the undistorted lattice at volume $V$, $\Delta V$ is the change of the volume due to the strain, and $O[\epsilon_i^3]$ are the neglected terms. For cubic systems, the elastic constants $C_{ij}$ reduce to three independent values, $C_{11}$, $C_{12}$, and $C_{44}$. By applying a volume conserving orthorhombic strain to the cubic lattice defined by

\[
\begin{align*}
\epsilon_1 &= -\epsilon_2 = x, \\
\epsilon_3 &= x^2 / (1 - x^2), \\
\epsilon_4 &= \epsilon_5 = \epsilon_6 = 0
\end{align*}
\] (2.26)

the change in the value $(C_{11} - C_{12})$ varies linearly to $x^2$

$$E = E_0 + V (C_{11} - C_{12}) x^2 + O[x^4]$$ (2.27)
where $x$ is the strain. In a similar way, by applying another volume conserving orthorhombic strain to the lattice defined by

\begin{align*}
é_6 &= x, \\
é_3 &= x^2 / (4 - x^2), \\
é_1 = é_2 = é_4 = é_5 &= 0
\end{align*}

the change in the value $C_{44}$ varies linearly to $x^2$

\begin{equation}
E = E_0 + \frac{1}{2} V C_{44} x^2 + O [x^4]
\end{equation}

where again $x$ is the strain. In both cases, $V$ is the constant volume of the lattice and $E_0$ is the value of the energy at that unstrained volume. So, after sampling the energies along the proper strain axis, a linear fit is done to obtain the values for $C_{11} - C_{12}$ and $C_{44}$. The bulk modulus is calculated by examining the $2^{nd}$ derivative of the change in energy as the volume changes.

\begin{equation}
B = -V \frac{d^2 E}{dV^2}
\end{equation}

A cubic material is mechanically stable if the three values $B$, $C_{11} - C_{12}$ and $C_{44}$ are positive.

\begin{align*}
B &= (C_{11} + 2C_{12}) / 3 > 0, \\
C_{11} - C_{12} &> 0, \text{ and} \\
C_{44} &> 0
\end{align*}

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2.13 Density of States (DOS)

The density of states (DOS) expresses the number of states per unit of energy. Accurate calculation of the DOS involves interpolation of the energies in k-space. A common procedure used to do the interpolation is the tetrahedron method.[21] In this method, the interpolation is done between four k-points which are at the vertices of a tetrahedron. The vertices are defined as

$$\epsilon(k) = \epsilon_0 + \bar{b} \cdot (\vec{k} - \vec{k}_0)$$  \hspace{1cm} (2.32)

where $\epsilon_0$ and $\bar{b}$ are determined from the corners of the tetrahedron. The DOS can be used to compute several properties which can be verified by experiment. Among those properties are the electronic component of the specific heat and the internal energy. The specific heat is defined as

$$C = \gamma T + \alpha T^2$$  \hspace{1cm} (2.33)

where the first term is the electronic contribution and the second term is the phonon contribution. $\gamma$ is the electronic specific heat coefficient and it is proportional to the density of states at the Fermi Level

$$\gamma = 0.1734 (1 + \lambda) N (\epsilon_F)$$  \hspace{1cm} (2.34)

where $\lambda$ is the electron-phonon coupling parameter and the units for $\gamma$ are $\frac{mJ}{mol \text{deg}^2}$. The density of states times the probability distribution function defines the number of occupied states per unit volume at a given energy. Given a density of states for the energy and a particular probability distributions the internal energy would be defined as

$$U = \sum E f_{BE}^{FD} (E) N(E) dE$$  \hspace{1cm} (2.35)

where $f_{BE}^{FD}$ represents either the the standard Fermi-Dirac or Bose-Eistein distributions and $DOS(E)$ is the DOS at the appropriate energy level.
2.14 Enthalpy

Enthalpy represents the total energy of a system and is defined as

\[ H = E + pV \]  \hspace{1cm} (2.36)

where \( H \) is the enthalpy, \( E \) is the total energy of the system, \( p \) is the pressure of the system and \( V \) is the volume of the system. Similar to when we examine the change in energy under different lattice sizes to determine the minimum lattice constant and deduce that the most stable configuration is the one with lowest energy, the examination of an enthalpy graph for various structures under pressure will show if the most stable structure for an element changes under pressure. The structure with the lowest enthalpy at a particular temperature would be predicted to be the most stable structure.

2.15 Vacancy Formation Energy

Vacancy formation energies will be calculated using the supercell approach.\(^7\) In this method a large lattice of atoms is constructed and the center cell is removed and the remaining atoms are allowed to relax around this position or are forced to remain fixed at their locations. Unrelaxed solutions will be higher than relaxed solutions. The vacancy formation energy is computed by comparing the energy of the system with and without the defect.

\[ E_{vf} = E(N - 1, 1) - \left( \frac{N - 1}{N} \right) E(N, 0) \]  \hspace{1cm} (2.37)

where \( E(N, M) \) is the energy of the lattice with containing \( N \) atoms and \( M \) vacancies. For purposes of this investigation a supercell of 125 atoms was used for the calculations. So, one calculation will have 125 atoms (\( N=125 \)) and zero vacancies (\( M=0 \)) and a second calculation will have 124 atoms (\( N=124 \)) and one vacancy (\( M=1 \)). The prediction is that energy of the system with a vacancy would be proportional to the total number of atoms remaining in...
the system. The critical feature of the vacancy formation is that a positive value indicates that the structure is more stable in the complete crystal structure than with a vacancy.

2.16 Phonons

Phonons are descriptions of the normal frequency modes of the crystal. The phonon frequencies of the material will be determined by the “frozen” phonon method.[22] In this method a supercell similar to the one used for the vacancy formation calculations is computed and atoms are displaced in a specified polarization direction.[23] The value of the phonon frequency describes vibrational mode of the lattice in that direction. To calculate the phonon frequency, several energies for the atom displacement are calculated an then the resulting data is fit to the energy data. The phonon frequency is determined by the value of the first derivative of the energy with respect to the displacement of the atoms from their equilibrium lattice positions. In the harmonic approximation, equation 2.38 is used

$$E = \frac{1}{2} \sum_{R, R', \alpha, \beta} u^\alpha (R) C^{\alpha \beta} \left( R - R' \right) u^\beta \left( R' \right)$$  \hspace{1cm} (2.38)$$

where $u^\alpha$ is the displacement from equilibrium of atom $\alpha$ on a unit cell associated with lattice vector $R$ and $C^{\alpha \beta} \left( R - R' \right)$ is the force constant connecting the displacement of the atom at $R$ in the $\alpha$ direction to the displacement of the atom at $R'$ in the $\beta$ direction. As an example of the workings of the harmonic approximation in the frozen phonon approach, we consider a two-atom unit cell such as the one used to determine the phonon frequencies along the delta line in the fcc material. For a displacement $d$ the kinetic energy for each atom is $\frac{1}{2} m d^2$ and the potential energy is $\frac{1}{2} k d^2$. Therefore, the constant total energy of the
two atoms is

\[
E = md^2 + kd^2
\]

\[
\dot{E} = 2m\ddot{d}d + k\dot{d}d = 2\ddot{d} \left( m\ddot{d} + kd \right) = 0
\]

This gives the equation for simple harmonic motion: \( \ddot{d} + \frac{k}{m}d = 0 \) and the frequency is

\[
\omega = \sqrt{\frac{k}{m}}.
\]

Now, if we write \( PE(d) = E_0 + kd^2 \), this means that \( PE'' = 2k \).
Chapter 3: Expansion of the NRL Tight-Binding Program

3.1 Original NRL Tight-Binding (TB) Program

The original NRL TB program uses the s, p and d-orbitals. The p-orbitals are expressed as x, y, and z; while, the d-orbitals are split into the $t_{2g}$ orbitals, yz, zx, and xy, and the eg orbitals, $x^2 - y^2$ and $3z^2 - r^2$. Thus, the secular equation to be diagonalized is a 9x9 matrix. As describe earlier, the Slater-Koster Tight Binding method bypasses solving of the integrals in the secular equation, and instead treats them as disposable parameters (equation 2.22) These parameters are determined by fitting to eigenvalues and total energies of first-principles results such as APW or LAPW. Once the best parameters are found, the eigenvalues and total energies can be determined for any structure. The NRL Tight Binding method extended the Slater-Koster (SK) implementation by introducing distance dependent polynomials for each SK parameter. The advantage of this implementation is that properly chosen Tight Binding polynomial coefficients are transferable to the study of other structures. There are three applications associated with the NRL TB package: the fitting application, the static application, and the molecular dynamics application. For this investigation only the fitting and static code were expanded.

Normally, the total energy of our lattice system would be written as

$$E = \sum_i f(\mu - \epsilon_i) \epsilon_i + F[\eta(r)]$$

(3.1)

where $\eta(r)$ is the electronic density, $\epsilon_i$ is the Kohn-Sham eigenvalue of the $ith$ electronic state, $\mu$ is the chemical potential and $F[\eta(r)]$ is defined by the non-kinetic energies terms
from equation 2.1

\[ F[\eta(r)] = E_{c-e}[\eta] + E_{c-n}[\eta] + E_{n-n}[\eta] + E_{xc}[\eta] \] (3.2)

However, since the Kohn-Sham method allows for an arbitrary shift in the potential, the NRL Tight-Binding method shifts the LAPW eigenvalues so that the total energy of the shifted eigenvalues will match the total energy.\[8\] The shifted eigenvalues are defined as

\[ \epsilon'_i = \epsilon_i + V_0 \] (3.3)

where the shift is

\[ V_0 = F[\eta(r)] / N_e \] (3.4)

where \( N_e \) is the number of valence electrons. By incorporating this shift, the total energy (3.1) becomes

\[ E = \sum_i f \left( \mu'_i - \epsilon'_i \right) \epsilon'_i \] (3.5)

The NRL Tight Binding Hamiltonian consists of matrix elements which are calculated from two types of interactions onsite integrals and two-center hopping integrals. In addition to simplifying the calculations, the exclusion of the three-center and crystal field integrals also improves the transferability of the resulting NRL-TB coefficients to other structures and volumes. The onsite terms appear only in the diagonal elements of the Hamiltonian matrix. In the NRL Tight Binding program, the s, p, and d electron interactions are split into four onsite integrals labeled s, p, t2g, and eg. These integrals are written in a polynomial form which depend on the density of the atoms, \( \rho \). The angular momentum dependent onsite terms equation is

\[ h_{il} = a_i + b_i \rho^{2/3} + c_i \rho^{4/3} + d_i \rho^2 \] (3.6)
where $a$, $b$, $c$, and $d$ are fitting coefficients. The atom density for a system is defined as

$$\rho_i = \sum_j \exp \left( -\lambda^2 R_{ij} \right) F(R_{ij})$$

(3.7)

where $\lambda$ is an additional fitting coefficient and $F(R_{ij})$ is a cutoff function to limit the number of neighboring atoms. The $F(R)$ is expressed as

$$F(R) = \theta \left( \frac{R_c - R}{\ell} \right) 1 + e^{\frac{(R - R_c)}{\ell}}$$

(3.8)

where $\theta(z)$ is the step function. For our analysis, $R_c$ was set to 16.5 and $\ell$ to 0.5 Bohr. So, with the initial $\lambda$ coefficient and four coefficients for each onsite integral, s, p, $t_{2g}$, and eg, a total of 17 coefficients are needed to define the onsite integrals in the NRL Tight-Binding method. Note, although $t_{2g}$ and eg have been specified as separate onsite integrals, in practice these terms are set equal to each other to avoid complications in transferability with non-cubic crystal structures.

The two-center integral introduces two contributions: hopping values which describe the energy of an electron "hopping" from one site to another and overlap integrals which define the interaction of non-orthogonal orbitals. In the case of a binary system, the number of two-center integrals in the original TB program would be 14

$$ss\sigma, sp\sigma, sd\sigma, ps\sigma, pp\sigma, pp\pi, pd\sigma, pd\pi, ds\sigma, dp\sigma, dp\pi, dd\sigma, dd\pi, dd\delta$$

If both atoms are the same, symmetry considerations remove four of the integrals

$$sp\sigma = -ps\sigma, sd\sigma = ds\sigma, pd\sigma = -dp\sigma, pd\pi = -dp\pi$$

So, for the monatomic case, there are ten independent integrals which needed to be considered. Each of these ten integrals is written as a distance dependent function with the
following form

\[ H_{\mu \mu} = (e_{\mu} + f_{\mu} R + g_{\mu} R^2) \exp \left( -h_{\mu}^2 R \right) F(R) \]  

with a similar expression for the overlap matrix. \( R \) represents the distance between two atoms and \( F(R) \) is the same cut-off function as described earlier. The coefficients in equation 3.9 are disposable parameters to be determined by the fitting to the LAPW results. With this way of defining the parameters, four new coefficients are needed for each original two-center SK parameter; so, the number of coefficients needed to define the hopping and overlap interactions is 80, four coefficients for each of the 10 hopping and 10 overlap equations. In summary, 97 coefficients are needed to build the complete non-orthogonal onsite and two-center integrals in the monatomic case, 17 for the onsite contributions and 80 for the two-center contributions.

The NRL Tight-Binding program uses a Levenberg-Marquardt least squares algorithm to minimize the total energy and eigenvalue differences between the TB and first-principles calculations. Mathematically we are trying minimize a weighted combination of the eigenvalues and the total energy differences

\[
\text{Minimize} \left[ \sum_s \left( W_s \left( E_{sTB} - E_{sLAPW} \right)^2 + \sum_k \sum_b w_{sb} \left( \epsilon_{skb}^{TB} - \epsilon_{skb}^{LAPW} \right)^2 \right) \right]^{1/2}
\]  

where the minimization is over all structures, k-points, and bands in the database, \( W_s \) is a weighting factor for the total energy value for structure s, \( w_{sb} \) is the weighting factor for structure s’s eigenvalue in band b, and the subscript \( skb \) denotes the eigenvalue for structure s’s k-point k and band b. In general, we only include in the minimization eigenvalues for the structures near the equilibrium lattice constant. The fitting process concludes due to one of several possible reasons: maximum number of fitting attempts completed, slow convergence detected, or desired error accuracy achieved. Because of the potential mixing
of orbital character, symmetry at several key k-point locations will be exploited to improve
the accuracy of the fit. If the results from a single Tight Binding fitting run do not meet
the desired minimum error, the calculated coefficients from that run can be used as the
starting point for a new Tight Binding run so that the desired fit accuracy can be achieved.
Because there is no guarantee that a good fit will be achieved, the process of finding a fit
involves intuition as well as science.

3.2 Initial Expansion of the NRL Tight-Binding Program

The expansion of the tight-binding program involved the inclusion of the f-orbitals. The f-
orbitals are represented by the equations

\[ (5z^2 - 3r^2)z, \quad (5z^2 - r^2)x, \quad (5z^2 - r^2)y, \quad (x^2 - y^2)z, \]

\[ (2xyz), \quad (x^2 - 3y^2)x, \quad \text{and} \quad (3x^2 - y^2)y. \]

The inclusion of these 7 f-orbitals expands our earlier Hamiltonian from a 9x9 matrix to a 16x16 matrix.

The first update to the program was to expand the onsite integral expressions in 3.6. The
addition of the f orbitals adds one additional onsite integral to the calculations. Following
the NRL Tight-Binding scheme, this additional integral will actually add four additional
fitting coefficients. This raises the number of onsite fitting coefficients from 17 to 21.

The second update to the program was to expand the computation of the hopping and
overlap integrals. The addition of the f-orbitals introduces 16 more integrals to the fitting
process as follows

\[ sf\sigma, pf\sigma, pf\pi, df\sigma, df\pi, ds\sigma, fp\sigma, fp\pi, fd\sigma, fd\pi, f\delta, f\gamma. \]

However, in the case of a monatomic material, only ten of those integrals are unique since

\[ sf\sigma = -fs\sigma, pf\sigma = fp\sigma, pf\pi = fp\pi, df\sigma = -fd\sigma, df\pi = -fd\pi, df\delta = -fd\delta. \]

So, the inclusion of the f orbitals means that for the monatomic case an additional ten
parameters are needed to define the hopping integrals and another ten parameters for
the overlap integrals. Again, following the NRL Tight-Binding scheme, each additional parameter will require 4 fitting coefficients. This raises the number of hopping and overlap fitting coefficients from 80 to 160. In summary, the total number of NRL Tight-Binding coefficients to account for s, p, d and f orbitals is 181; 21 coefficients to model the onsite integrals and 160 coefficients to model the hopping and overlap integrals.

In the original version of the NRL Tight-Binding program, the 9x9 Hamiltonian matrix was computed by evaluating a series of hard-coded equations as described in Table I of the Slater-Koster paper.[3]. To extend this scheme to f orbitals, the 9x9 Hamiltonian matrix was expanded to a 16x16 matrix to account for the additional f-orbitals. Further, the equations required to populate the new matrix elements needed to be determined. In a paper by Lendi[4], the equations for the additional matrix elements are described in Table I of this paper. To incorporate the equations from the Lendi paper required the proper mapping of Lendi’s rotation of orbitals to what existed in the NRL Tight-Binding program.

The generation of the Hamiltonian matrix involves the computation of overlap integrals associated with the lattice of the material being investigated. Each element of the Hamiltonian matrix is defined by

\[
H_{ij} = \sum_v \sum_{R_v} e^{\vec{k} \cdot \vec{R}_v} E_{vij}^
u
\]  

(3.11)

where \( \vec{R}_v \) is the set of \( v^{th} \) nearest neighbors and \( E_{vij} \) is the overlap matrix between orbital i and orbital j. Following Lendi’s notation, the 16 orbitals in Cartesian notation are shown in Table 3.1. The s, p, d and f functions in Table 3.1 are derived from the spherical harmonics definition

\[
Y_{lm}^m(\omega, \phi) = \sqrt{\frac{2l + 1}{4\pi} \frac{(l - m)!}{(l + m)!}} P_{li}^m e^{im\phi}
\]  

(3.12)

As we can see in Table 3.1, the order of the orbitals in Lendi’s expansion and the order of the orbitals in the NRL-TB program were different. During the integration of the new
Table 3.1: Cartesian Orbital Coefficients

<table>
<thead>
<tr>
<th>TB Index</th>
<th>Orbital</th>
<th>Cartesian Basis Function</th>
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</thead>
<tbody>
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<td>S</td>
</tr>
<tr>
<td>2</td>
<td>$(3/4\pi)^{1/2}x$</td>
<td>$P_1$</td>
</tr>
<tr>
<td>3</td>
<td>$(3/4\pi)^{1/2}y$</td>
<td>$P_2$</td>
</tr>
<tr>
<td>4</td>
<td>$(3/4\pi)^{1/2}z$</td>
<td>$P_0$</td>
</tr>
<tr>
<td>5</td>
<td>$(60/16\pi)^{1/2}yz$</td>
<td>$D_2$</td>
</tr>
<tr>
<td>6</td>
<td>$(60/16\pi)^{1/2}xz$</td>
<td>$D_1$</td>
</tr>
<tr>
<td>7</td>
<td>$(60/16\pi)^{1/2}xy$</td>
<td>$D_4$</td>
</tr>
<tr>
<td>8</td>
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<td>$D_3$</td>
</tr>
<tr>
<td>9</td>
<td>$(5/16\pi)^{1/2}(3z^2 - r^2)$</td>
<td>$D_0$</td>
</tr>
<tr>
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<td>$F_0$</td>
</tr>
<tr>
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<td>$F_1$</td>
</tr>
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<td>12</td>
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<td>$F_2$</td>
</tr>
<tr>
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<td>$F_3$</td>
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<tr>
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</table>

Formulas, it was important to be consistent in the indexing. Once the mapping of orbitals was determined it was a straight-forward, if tedious, process to include the new formulas. Two problems occurred with this initial implementation of Lendi’s formulas provided by Lendi. First, the f-f orbital interactions were not included in his derivation because he felt the contributions from those orbital interactions would be negligible. Second, while testing the expanded NRL TB program, it was noticed that there was a problem with the matrix elements; the expanded matrix was not computing the original set of eigenvalues in addition to the new eigenvalues. This led to a more rigorous investigation into computation of the formulas themselves and confirmed mistakes in the formulas also found by others, notably Sharma. In addition to providing corrected formulas, Sharma’s investigation included a list of the missing f-f orbital interactions. However, the fact that the original expansion had errors and that it was shown that the manual entry of the formulas could lead to errors, it was decided that utilizing an automated way to generate the orbital coefficients would be preferable to hard coding the equations. The compact expression for computing the orbital
interaction coefficients was provided by Podolskiy and Vogl.

### 3.3 Formula Expansion of the NRL Tight-Binding Program

In a paper by Podolskiy and Vogl, a compact expression to compute the Hamiltonian matrix elements is described.[6] We are examining the interaction between two atoms. For simplicity, we will define the origin of the system at the position of one of the atoms. In this system, the directional cosines \((L, M, N)\) define the line connecting atom 1 which is at the origin of the system to the second atom. At each atom there will be a set of independent spherical harmonics, \(Y_{l,m}(\theta, \phi)\). Additionally, it is useful to define a set of rotated spherical harmonics, \(Y_{l,m}^{\xi}(\theta_\xi, \phi_\xi)\), relative to the \(R_\xi\) axis connecting the two atoms. In the rotated system we can define two Euler angles, \(\beta\) and \(\gamma\) which relate the original direction cosines \((L, M, N)\). The equations relating the Euler angles to the Cartesian coordinates are shown in 3.13 with the third Euler angle set to zero. A visual representation of the system is shown in Figure 3.1.

\[
\begin{align*}
\cos(\beta) &= N, \\
\sin(\beta) &= \sqrt{1 - N^2}, \\
\sin(\gamma) &= \frac{M}{\sqrt{1 - M^2}}, \\
\cos(\gamma) &= -\frac{L}{\sqrt{1 - M^2}}
\end{align*}
\]  

(3.13)
The relationship between the old and new spherical harmonics is

\[ Y_{l,m}^{\xi}(\theta, \phi) = \sum D_{m',m}^{l}(\beta, \gamma) Y_{l,m'}^{\xi}(\theta, \phi), \]

where

\[ D_{m',m}^{l}(\beta, \gamma) = \langle lm|R(\beta, \gamma)|lm'\rangle = e^{i\gamma m'} d_{m',m}^{l}(\beta) \]

and

\[ d_{m,m'}^{l} = \left( \frac{1 + N}{2} \right)^{l} \left( \frac{1 - N}{1 + N} \right)^{m-m'} \]

\[ \left[ (l + m')! (l - m')! (l + m)! (l - m')! \right]^{1/2} \]

\[ \sum_{t=0}^{2l+1} \left[ \frac{(-1)^{t}}{(l + m' - t)! (l + m - t)! t! (l + m - m')!} \left( \frac{1 - N}{1 + N} \right)^{t} \right] \]

note: the summation is for all non-negative factorials

Within the method, real basis orbitals are considered in the tight binding method and tesseral spherical harmonics were used in the solution process. The equations relating the
tesseral and complex spherical harmonics are

\[ Y_{l,0}(\theta, \phi) = Y_{l,0}(\theta, \phi) \]

\[ m > 0 : Y_{l,m}(\theta, \phi) = \sqrt{2} (-1)^m \text{Re} Y_{l,m}(\theta, \phi) \] (3.15)

\[ m < 0 : Y_{l,m}(\theta, \phi) = \sqrt{2} (-1)^m \text{Im} Y_{l,m}(\theta, \phi) \]

With the above definition, the basis orbital functions become

\[ \langle r | l, m, R \rangle = Y_{l,m}(\theta, \phi) \rho(|r - R|) \] (3.16)

where \( \rho \) is the radial component at site \( R \) and the Hamiltonian matrix elements become

\[ \langle l_1, m_1, 0 | H | l_2, m_2, R_\xi \rangle = \int dr Y_{l_1,m_1}(\theta, \phi) \rho_1(|r|) H Y_{l_2,m_2}(\theta, \phi) \rho_2(|r - R_\xi|) \] (3.17)
Upon integration, the analytic equations for the Hamiltonian matrix elements are

\[
\langle l_1, m_1, 0 | H | l_2, m_2, R \xi \rangle = (-1)^{(l_1 - l_2 + |l_1 - l_2|)} / 2
\]

\[
\left\{ \sum_{l', m'} \left[ S_{l_1, m_1, l_2, m_2, l'}^{l_1} S_{m_1, m_2, l'}^{l_2} + T_{l_1, m_1, l_2, m_2, l'}^{l_1} (l < l') \right] \right\}
\]

\[
+ 2A_{m_1} A_{m_2} d^{l_1}_{m_1, 0} d^{l_2}_{m_2, 0} (l < l > 0)
\]

\[
S_{m_1, m_2}^{l_1} = A_m \left[ (-1)^{|m'|} d^{l_1}_{m_1, m_2, m_2} + d^{l_1}_{m_2, m_1, m_2} \right]
\]

\[
T_{m_1, m_2}^{l_1} = (1 - \delta_{m_0}) B_m \left[ (-1)^{|m'|} d^{l_1}_{m_1, m_2, m_2} - d^{l_1}_{m_2, m_1, m_2} \right]
\]

\[
A_m = (-1)^{|m|} \left[ \tau (m) \cos (|m| \gamma) - \tau (-m) \sin (|m| \gamma) \right]
\]

\[
B_m = (-1)^{|m|} \left[ \tau (m) \sin (|m| \gamma) - \tau (-m) \cos (|m| \gamma) \right]
\]

\[
\tau (m) = 1 \text{ if } m \geq 0 \text{ or } 0 \text{ if } m < 0
\]

The \( \langle l_1, m_1, 0 | H | l_2, m_2, R \xi \rangle \) represents the two-center Hamiltonian matrix elements. The \((l_1, l_2, |m|)\) and \((l_1, l_2, |m|)\) factors in the Hamiltonian matrix elements are place holders for low level integrals which will be replaced by disposable parameters during the fitting process.

A modification was introduced by Hourahine which removes the singularity associated with the ‘d’ equation.\[11\]

\[
d^{l_1}_{m_1, m_2} = 2^{-l} \left[ (l + m')!(l - m')!(l + m)!(l - m)! \right]^{1/2}
\]

\[
\sum_{t=0}^{2l+1} \left[ (1 - N)^{2l+m-m'} / 2 (1 + N)^{2l-2l-m+m'} / 2 \right]^{-1/2}
\]

\[
\frac{-1^t}{(l + m' - t)! (l + m - t)!(l + m - m')!}
\]

note: the summation is for all non-negative factorials

31
Computing the Hamiltonian matrix elements in this fashion increases the speed of the program, it also minimized the likelihood of error in the coding of the Hamiltonian matrix elements. In addition, the general method will have the advantage of allowing the program to be extended to include g-orbitals easily.

3.4 Block Diagonalization

Block diagonalization is a process by which using crystal symmetry a larger matrix is transformed into a set of smaller matrices which produce the same eigenvalues as the original matrix. In particular, if a matrix has rows and columns which are linearly independent, those sub-matrices can be solved separately from the full matrix. In our situation, at high symmetry points using the crystal symmetry, the full Hamiltonian matrix can be ‘broken down’ into smaller blocks which are easier to solve and ensure that the proper eigenvector character is achieved. During the expansion of the NRL tight-binding program, the block diagonalization of the original program had to be modified to account for the mixing of f-orbital character with s, p, and d orbitals. To determine the block diagonalization, the matrix of values is examined. In some cases, additional rotations or linear combinations of the matrix elements are done.

For the Γ point the matrix elements are shown in Figure 3.2a. Several diagonal blocks can be observed in this matrix. There is a single block with pure s characteristic at $H_{1,1}$, a triply degenerate block with pure t2g-d symmetry encompassing $H_{5,5}, H_{6,6}, H_{7,7}$, a doubly degenerate block with pure eg-d symmetry encompassing $H_{8,8}, H_{99}$, a single block with pure f character at $H_{14,14}$, and then three 3x3 sub-matrices from the remaining matrix elements which mixed p and f character. In the original NRL-TB program, the original block diagonalization for the p character elements did not have to account for the mixing of p and f characteristics; so, the original block diagonalization, though appropriate for a 9x9 matrix, would not work with the new 16x16 matrix. It is important to note, the each of the 3 remaining 3x3 matrices each produce the same three eigenvalues.

The next k-point examined was the X point shown in Figure 3.2b. Like the Γ matrix,
this matrix did not require any additional manipulation to reduce the matrix to a diagonal set of blocks. From Figure 3.2b we can see block (1,9) with s and eg-d character, a doubly degenerate 3x3 set of matrices represented by blocks (2,11,15) and (3,12,16) with p and f character, block (4,10) with p and f character, a doubly degenerate d character value in block (5,5), single d character values in blocks 7 and 8, and single f character values in blocks 13 and 14.

The last k-point examined was the L point shown in Figure 3.2c. As can be seen in Figure 3.2c, there is significant mixing of orbitals across the entire matrix. From examining the original NRL-TB program it was seen that the matrix was rotated 45 degrees around the (2,3) and (5,6) axes to achieve block diagonalization. With the addition of the f orbitals, it was determined that the matrix additional 45 degree rotations around the (11,12), and (15,16) axes would help decouple some of the matrix elements. With those four rotations, the L matrix transforms to Figure 3.2d. Viewing the rotated L matrix, it is easy to see that there are 5 blocks within the 16x16 matrix, block (1,6,7,9) with s and d character, block (2,11,13,16) with p and f character, block (3,4,10,12,14,15) with p and f character, and block (5,8) with pure d character.

The results of our inspections of Figure 3.2 are summarized in Table 3.2.

### 3.5 Expanded Program Testing and Validation

During the expanding of the code from spd to spdf, certain validation steps were performed to verify that the updated code was working properly. The first validation step was to check that the expanded program returned the same results as the original program when only considering s, p, and d orbitals. Both the band errors and the energy values were examined to determine if the new code was behaving properly. Both orthogonal and non-orthogonal tests were performed. To verify the code, the band RMS error, total energy, and total energy RMS errors were examined and were shown to be in agreement. Additional tests were made with the block diagonalization changes to verify that the same eigenvalues were computed.
Figure 3.2: Block Diagonalization Matrices

(a) Γ

(b) X

(c) L Unrotated

(d) L Rotated
Table 3: Block Diagonalization for high-symmetry K-points, L, X, and I

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for both a full matrix and the smaller matrices resulting from the block diagonalization.

### 3.6 Speed Improvements

While trying to investigate our first material, the simple analytic computation of the matrix elements was extremely slow. This limitation made it difficult to examine materials quickly because the time to generate test fits was too long. In examining, the initial implementation of the analytic process, it was noted that many of the coefficients associated with the formulas are zero. This insight led to a modification of the initial implementation which kept a map of the non-zero coefficients needed to calculate a matrix element. By looping over only the needed non-zero coefficients, the program speed was improved by more than a factor of ten.

### 3.7 Fitting Process

The modified Tight-Binding program was used to generate a set of TB coefficients for examining the electronic structure of Thorium and Actinium. During the fitting process three kinds of input data were considered. All of this data were obtained from first-principles LAPW calculations. The first kind of data to fit were energy bands; these are the eigenvalues at specific points in the Brillouin zone. A good band fit is said to be achieved when there is an average RMS error on the order of 10 mRy for all bands under consideration. The second kind of data to fit were the total energy for various structures, both near and away from the equilibrium structure minimum. The number of k-points in the Brillouin zone which must be sampled depends on the structure. The number of k-points used were: fcc - 89 k-points, bcc - 55 k-points, sc - 35 k-points, and for diamond - 89 k-points. These four crystal structures ensure that the energy ordering is correct. The desired total energy RMS error is on the order of 2 mRy across all structures under consideration. During the construction of the input files, the energy values for the structures are shifted relative to the lowest structure energy.
The last fitting data will be the block diagonalized Hamiltonian at high symmetry points \( \Gamma, X, \) and \( L \) for the fcc structure as shown in Table 3.2. As has been pointed out in the book [24] by Papaconstantopoulos and his review article with Mehl [7], it is important to include block-diagonalization to avoid the incorrect assignment of eigenvalues to angular momentum character and symmetry. This point was also emphasized by Jones and Albers [9].

The iterative process for attempting to determine a set of transferable coefficients for a given structure is:

1. Run first principles calculation (LAPW) to compute total energy and energy bands for the most stable structure and other structures (e.g. fcc, bcc, sc, dia, ...). It is important to include data from not only the minimum energy lattice spacing for a structure, but also for other lattice constants near the structure minimum.

2. Construct a set of starting TB coefficients choosing the on-sites from the LAPW values at the \( \Gamma \) point and setting the hopping parameters to very small values.

3. Start the fitting process by using data from three lattice constants near the best minimum energy lattice spacing for the ground energy structure (fcc or bcc) and one lattice constant at the other minimum energy lattice spacing.

4. Include block diagonalization information at points of high symmetry.

5. After an acceptable fit from the subset of data is achieved, gradually add additional sets from other lattice constants.

6. As necessary reset and freeze coefficients to improve the fitting process.

7. Once a complete TB fit set of coefficients is found, use the static program to compute band structure and other properties of the materials (i.e. elastic constants, phonon frequencies, ).

8. Compare the computed static values and graphs to LAPW results and experimental data.
Although our computer code is designed to derive the coefficients for a non-orthogonal Hamiltonian as well, in the present work we did not include the overlap matrix which reduced the number of disposable two-center coefficients fit to 80. Between the exclusion of the overlap integrals and the simplification in the onsite integral coefficients by setting $t_{2g}$ equal $e_g$, a total of 97 fitting coefficients were used. Even with this reduced set of coefficients, a good fit was obtained.
Chapter 4: Thorium

4.1 Introduction

There have been several investigations into the properties of Thorium and even early attempts to produce a set of Tight-Binding parameters to describe the behavior of the material. There also has been specific research done to compare analytic phonon properties of Thorium to experimental results. However, to date, no complete set of transferable parameters have been developed for this material which could produce predictions for both material behavior and phonon information. This section of the paper will describe how the modified NRL-TB program was used to create a robust set of transferable NRL-TB parameters which accurately reproduce the LAPW results associated with the total energies and band structure and in addition predict vacancy formation energy and phonon frequencies.

4.2 Computational Details

For Thorium, full-potential, scalar relativistic LAPW total energy calculations were done using the GGA treatment of exchange and correlation. The resulting equilibrium lattice parameter was in excellent agreement with the experimental value of $a = 9.60$. These calculations were used to create a target database of energies and band structure across a set of lattice constants and lattice types near Thorium’s theoretical equilibrium volume at the fcc lattice value 9.6 Bohr. Specifically, 18 fcc structures ranging from 8.0 to 10.8 Bohr, 5 BCC structures ranging from 7.2 to 8.6 Bohr, 5 SC structures ranging from 5.6 to 7.0, and 5 diamond structures from 13.0 to 14.5 Bohr were fit. Using this database of 33 structures and lattice constants, we reproduce very well the LAPW results and also predicted correctly the position of the hcp lattice and found the A15 and L12 structures at high energies.
However, upon running the elastic constant tests, we found negative values violating mechanical stability. This error in the predictions associated with the elastic constants led to the inclusion of the elastic constants themselves in the fit. LAPW $C_{11} - C_{12}$ and $C_{44}$ results were included in the fit so that a mechanically stable set of results could be achieved. After it appeared a good fit had been found for the total energies, bands, and elastic constants, the examination of the phonons revealed that some imaginary phonon frequencies were being predicted. This problem was corrected by adding to the fitting database additional band information at the equilibrium lattice location. The addition of fitting directly to the full band data information corrected the rest of the non-physical results and it was then possible to obtain a set of coefficients for use with the "static" component of the NRL TB package.

### 4.3 Tight-Binding Fit

Although both orthogonal and non-orthogonal fits can be performed using the NRL Tight-Binding program, only an orthogonal fit was done for this work. For the Thorium fit, the total energy error was 2 mRy as shown in Table 4.1 and the average band error across 11 bands at the equilibrium lattice location was 17 mRy as shown in Table 4.2. The band errors were a little higher than desired, but the fits did appear to produce reasonable results for all of Thorium’s properties. The best fit onsite coefficients had the additional restriction that the values for $t_{2g}$ and $e_g$ would be identical because the crystal field separation of $t_{2g}$ and $e_g$ is only applicable to the cubic symmetry which causes problems for the transferability to other structures. The onsite parameters influence the diagonal elements of the Hamiltonian matrix while the hopping parameters affect the off-diagonal elements. The complete set of onsite and hopping coefficients are shown in Tables 4.3.

The onsite Slater-Koster coefficients computed by Equation 3.6 of Section II using the coefficients from Table 4.3 as a function of the FCC lattice constant are shown in Figure 4.1a. The key feature of this graph is to note that the graphs are well behaved although the
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<td>0.0641</td>
<td>0.0649</td>
<td>0.0008</td>
</tr>
<tr>
<td>BCC</td>
<td>7.4</td>
<td>0.0149</td>
<td>0.0089</td>
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</tr>
<tr>
<td>BCC</td>
<td>7.6</td>
<td>0.0108</td>
<td>0.0099</td>
<td>-0.0009</td>
</tr>
<tr>
<td>BCC</td>
<td>8</td>
<td>0.0192</td>
<td>0.0286</td>
<td>0.0004</td>
</tr>
<tr>
<td>BCC</td>
<td>8.6</td>
<td>0.0759</td>
<td>0.0722</td>
<td>-0.0038</td>
</tr>
<tr>
<td>SC</td>
<td>5.6</td>
<td>0.0992</td>
<td>0.0994</td>
<td>0.0001</td>
</tr>
<tr>
<td>SC</td>
<td>6</td>
<td>0.0726</td>
<td>0.0701</td>
<td>-0.0025</td>
</tr>
<tr>
<td>SC</td>
<td>6.2</td>
<td>0.0659</td>
<td>0.0662</td>
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<tr>
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<td>0.0692</td>
<td>0.0023</td>
</tr>
<tr>
<td>SC</td>
<td>7</td>
<td>0.1028</td>
<td>0.1032</td>
<td>0.0004</td>
</tr>
<tr>
<td>DIA</td>
<td>13</td>
<td>0.1566</td>
<td>0.1564</td>
<td>-0.0002</td>
</tr>
<tr>
<td>DIA</td>
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<td>0.1488</td>
<td>0.1484</td>
<td>-0.0004</td>
</tr>
<tr>
<td>DIA</td>
<td>13.9</td>
<td>0.1483</td>
<td>0.1485</td>
<td>0.0002</td>
</tr>
<tr>
<td>DIA</td>
<td>14</td>
<td>0.1488</td>
<td>0.1489</td>
<td>0.0001</td>
</tr>
<tr>
<td>DIA</td>
<td>14.5</td>
<td>0.1557</td>
<td>0.1554</td>
<td>-0.0003</td>
</tr>
<tr>
<td>C11C12</td>
<td>1</td>
<td>0.0007</td>
<td>0.0003</td>
<td>-0.0004</td>
</tr>
<tr>
<td>C11C12</td>
<td>1</td>
<td>0.0014</td>
<td>0.0012</td>
<td>-0.0002</td>
</tr>
<tr>
<td>C11C12</td>
<td>1</td>
<td>0.003</td>
<td>0.003</td>
<td>0</td>
</tr>
<tr>
<td>C44</td>
<td>1</td>
<td>0.0004</td>
<td>0.001</td>
<td>0.0006</td>
</tr>
<tr>
<td>C44</td>
<td>1</td>
<td>0.0016</td>
<td>0.0029</td>
<td>0.0013</td>
</tr>
<tr>
<td>C44</td>
<td>1</td>
<td>0.004</td>
<td>0.0062</td>
<td>0.0022</td>
</tr>
</tbody>
</table>

Table 4.1: Thorium NRL-TB database for the structures and energies fit. The input energies, orthogonal fit energies and the difference between the input and output are shown. The overall energy RMS error of 0.0020 Ry across all structures is acceptable.
<table>
<thead>
<tr>
<th>Type</th>
<th>Lat Constant (Bohr)</th>
<th>Band</th>
<th>RMS Error (Ry)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FCC</td>
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<td>1</td>
<td>0.0099</td>
</tr>
<tr>
<td>FCC</td>
<td>9.6</td>
<td>2</td>
<td>0.025</td>
</tr>
<tr>
<td>FCC</td>
<td>9.6</td>
<td>3</td>
<td>0.0199</td>
</tr>
<tr>
<td>FCC</td>
<td>9.6</td>
<td>4</td>
<td>0.0169</td>
</tr>
<tr>
<td>FCC</td>
<td>9.6</td>
<td>5</td>
<td>0.0163</td>
</tr>
<tr>
<td>FCC</td>
<td>9.6</td>
<td>6</td>
<td>0.021</td>
</tr>
<tr>
<td>FCC</td>
<td>9.6</td>
<td>7</td>
<td>0.0143</td>
</tr>
<tr>
<td>FCC</td>
<td>9.6</td>
<td>8</td>
<td>0.0114</td>
</tr>
<tr>
<td>FCC</td>
<td>9.6</td>
<td>9</td>
<td>0.0103</td>
</tr>
<tr>
<td>FCC</td>
<td>9.6</td>
<td>10</td>
<td>0.0198</td>
</tr>
<tr>
<td>FCC</td>
<td>9.6</td>
<td>11</td>
<td>0.0178</td>
</tr>
<tr>
<td></td>
<td>Average RMS</td>
<td></td>
<td>0.0172</td>
</tr>
</tbody>
</table>

Table 4.2: Thorium Band fit at the FCC equilibrium lattice constant 9.6. Since each band has 85 points only the RMS error across all k-points in a band is shown. The overall energy RMS error of 0.0172 is a little high but acceptable.

<table>
<thead>
<tr>
<th>λ</th>
<th>1.02539</th>
</tr>
</thead>
<tbody>
<tr>
<td>On-site</td>
<td>a</td>
</tr>
<tr>
<td>s</td>
<td>0.13797</td>
</tr>
<tr>
<td>p</td>
<td>0.03488</td>
</tr>
<tr>
<td>t2g / eg</td>
<td>0.14610</td>
</tr>
<tr>
<td>f</td>
<td>0.08457</td>
</tr>
<tr>
<td>Hopping</td>
<td>e</td>
</tr>
<tr>
<td>sσσ</td>
<td>51.57930</td>
</tr>
<tr>
<td>spσ</td>
<td>32.36753</td>
</tr>
<tr>
<td>ppσ</td>
<td>-1.52404</td>
</tr>
<tr>
<td>ppσ</td>
<td>11.30628</td>
</tr>
<tr>
<td>sdσ</td>
<td>141.65242</td>
</tr>
<tr>
<td>pdσ</td>
<td>-69.21398</td>
</tr>
<tr>
<td>pdσ</td>
<td>24.52695</td>
</tr>
<tr>
<td>ddσ</td>
<td>102.95988</td>
</tr>
<tr>
<td>ddσ</td>
<td>2.96755</td>
</tr>
<tr>
<td>ddδ</td>
<td>10.58619</td>
</tr>
<tr>
<td>sfσ</td>
<td>-6.94685</td>
</tr>
<tr>
<td>pfσ</td>
<td>-35.98929</td>
</tr>
<tr>
<td>pfσ</td>
<td>-7.25622</td>
</tr>
<tr>
<td>dδσ</td>
<td>2.88063</td>
</tr>
<tr>
<td>dδσ</td>
<td>44.26243</td>
</tr>
<tr>
<td>dδσ</td>
<td>-128.52489</td>
</tr>
<tr>
<td>dδσ</td>
<td>-9.30697</td>
</tr>
<tr>
<td>dδσ</td>
<td>4.62519</td>
</tr>
<tr>
<td>dδσ</td>
<td>-14.73599</td>
</tr>
</tbody>
</table>

Table 4.3: The best fit Thorium coefficients. Since for the cubic structure t2g and eg we set to equal each other, only a single set of coefficients is computed for $t_{2g}$ and $e_g$. 


Figure 4.1: Onsite and Hopping integral graphs for Thorium. In the onsite graph shows that the f orbitals contribute significantly to the overall Hamiltonian. The two-center hopping integrals show all the energies asymptotically approaching zero although the change in direction for some of the graphs below 8 Bohr should be investigated further.

The fact that the p contribution to the energy is increasing with lattice size should be re-investigated. It is also interesting to note that the f onsite integral contribution to the overall Hamiltonian will be significant since its energy values are of the same magnitude as the other onsite contributions. The hopping Slater-Koster coefficients computed by Equation 3.9 of Section II using the coefficients from Table 4.3 as a function of the distance R are shown in Figure 4.1b. There are 20 hopping parameters, but we only show seven of them in Figure 4.1b to enhance the visibility of the graphs. All the functions asymptotically approaching zero as the distance increases, but some of the orbitals are exhibiting some potentially odd behavior. The fact that some curves change direction for radius values below 8 Bohr could warrant further investigation.

### 4.4 Ground-State Behavior and Phase Stability

Given the coefficients listed in Table 4.3, the NRL static program was used to examine the different lattice structures as shown in Figure 4.2. The value of determining a set of transferable fitting coefficients is seen in this example. For the same set of coefficients a variety of structures can be examined, ones which were fit (e.g. FCC, BCC, SC, DIA) and structures which were not fit (e.g. HCP, L12, and A15). It should be noted that before
Figure 4.2: Energy-volume behavior of Thorium across several different structures. All curves show a local minimum and are well behaved in the region plotted. In particular, FCC is seen to be the most stable structure since it has the minimum energy across all structures.

computing the fit for HCP, a side analysis of how HCP energy varied for different c/a ratios to determine the c/a ratio which would produce the lowest HCP energies. That analysis showed that a c/a ratio of 1.65 would produce the most stable configurations. A graph showing FCC compared to HCP at some c/a ratios at and near the equilibrium c/a for Thorium is shown in Figure 4.3. The L12 structure is similar to the AuCu3 structure and normally has four atoms in the unit cell; however, for the L12 structure the Au atom at the origin is removed. The positions for the other three atoms are at (0.00, 0.50, 0.50), (0.50, 0.00, 0.50), and (0.50, 0.50, 0.50). The A15 structure is also known as Cr3Si and has eight atoms in the unit cell. The positions for the eight atoms are (0.00, 0.00, 0.00), (0.50, 0.50, 0.50), (0.25, 0.50, 0.00), (0.75, 0.50, 0.00), (0.00, 0.25, 0.50), (0.00, 0.75, 0.50), (0.50, 0.00, 0.25), and (0.50, 0.00, 0.75). Computing a quadratic fit or birch fit to the static data, the minimum energy and corresponding lattice constant for each type of structure can be found. A summary of those minimum energy values and volumes and how they
Figure 4.3: The graphs show the Thorium HCP investigation to find the best c/a ratio to compute the HCP energies. The minimum energy for the HCP structure was found for a c/a ratio of 1.65 for the HCP volume 440.

The analysis confirms that FCC is the most stable structure since all other structures have higher minimum energies.

Another investigation into the stability of the fit would be to examine structures of lower symmetry. The Bain path, shown in Figure 4.4, shows the energy of Thorium under a volume conserving tetragonal strain. The curve properly shows that at the FCC structure location, the energy is a minimum and the BCC a maximum.

4.5 Elastic Constants

The elastic constants were computed as a by product of the Birch fit and by applying the appropriate volume conserving tetragonal or orthorhombic strains to the lattice. All three values, \( B \), \( C_{11} - C_{12} \), and \( C_{44} \) are positive values indicating the fcc structure is mechanically stable. The summary of the elastic constant information shows very good comparison to
Table 4.4: Comparison of LAPW and fit structure energies and volumes for Thorium. The c/a ratio of 1.65 for HCP was used since it would produce the minimum HCP energy across all c/a values. FCC is shown to be the most stable structure since it has the lowest energy.

<table>
<thead>
<tr>
<th></th>
<th>Th LAPW</th>
<th>Th TB</th>
</tr>
</thead>
<tbody>
<tr>
<td>SC</td>
<td>0.066 Ry</td>
<td>0.067 Ry</td>
</tr>
<tr>
<td></td>
<td>6.20 Bohr</td>
<td>6.24 Bohr</td>
</tr>
<tr>
<td>BCC</td>
<td>0.011 Ry</td>
<td>0.010 Ry</td>
</tr>
<tr>
<td></td>
<td>7.60 Bohr</td>
<td>7.48 Bohr</td>
</tr>
<tr>
<td>FCC</td>
<td>0.000 Ry</td>
<td>-0.001 Ry</td>
</tr>
<tr>
<td></td>
<td>9.60 Bohr</td>
<td>9.59 Bohr</td>
</tr>
<tr>
<td>DIA</td>
<td>0.148 Ry</td>
<td>0.148 Ry</td>
</tr>
<tr>
<td></td>
<td>13.90 Bohr</td>
<td>13.82 Bohr</td>
</tr>
<tr>
<td>HCP</td>
<td>-</td>
<td>0.002 Ry</td>
</tr>
<tr>
<td></td>
<td></td>
<td>c = 10.97 Bohr</td>
</tr>
<tr>
<td></td>
<td></td>
<td>c/a = 1.65</td>
</tr>
<tr>
<td>A15</td>
<td>-</td>
<td>0.027 Ry</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.13 Bohr</td>
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<tr>
<td>L12</td>
<td>-</td>
<td>0.034 Ry</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.17 Bohr</td>
</tr>
</tbody>
</table>

Figure 4.4: Tight-binding calculation of the energy of Thorium under a tetragonal strain (the Bain Path) as a function of c/a. The vertical lines denote the positions for the BCC and FCC lattices.
Thorium

<table>
<thead>
<tr>
<th></th>
<th>Experimental</th>
<th>LAPW</th>
<th>TB Ortho</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk</td>
<td>54.00 GPa</td>
<td>55.29 GPa</td>
<td>58.05 GPa</td>
</tr>
<tr>
<td>$C_{11} - C_{12}$</td>
<td>62.89 GPa</td>
<td>34.57 GPa</td>
<td>54.55 GPa</td>
</tr>
<tr>
<td>$C_{44}$</td>
<td>31.00 GPa</td>
<td>50.38 GPa</td>
<td>60.02 GPa</td>
</tr>
</tbody>
</table>

Table 4.5: Elastic constants for Thorium. The fact that all three elastic constants have positive values indicates that the fit is mechanically stable.

The experimental data for the bulk modulus and $C_{11} - C_{12}$, but has a very high error associated with $C_{44}$. Because Thorium is such a soft material with small elastic constant values, it can be difficult to get accurate predictions for these values. Also, in the case of $C_{44}$, we see that although the results do not fit experiment well, the results do match the LAPW results well. Part of the reason why the $C_{44}$ prediction matches the LAPW results well could be because some LAPW $C_{44}$ values were in the fitting database.

4.6 Electronic Structure

Both the TB bands and the density of states (DOS) match the related LAPW data for the FCC structure at equilibrium as shown in Figure 4.6a. This verifies the quality of the fit. In Figure 4.6a, we note that the occupied TB bands match the LAPW bands well along the $\Delta$, $Z$, and $Q$ directions but show some discrepancy along the $\Lambda$ and $\Sigma$ directions; however, a full 11 bands were fit well as supposed to just the bands below the Fermi level. We also see in the final DOS fit that the peaks in both the LAPW DOS and the TB DOS occur in the same relative locations. The position of the Fermi level agrees very well and the sharp peak indicating the f-states are also in agreement. Of particular interest is the $\Gamma_2'$ state. This band has pure f-character and is located near the Fermi level. It is this kind of f-orbital in influence which makes the integration of the f-orbitals into the calculations necessary to produce reliable predictions for Th and may also explain why there was some difficulty in actually fitting to the database of Th values. Using the DOS at the Fermi level and assuming that electron-phonon coupling, $\lambda$, is zero, an estimation for the electronic specific heat coefficient can be made using Equation 2.34. At the Fermi level, the DOS for
Figure 4.5: Energy graphs for determining the elastic constants of Thorium. The Bulk Modulus is determined by computing the partial derivative of the change in energy per volume. $C_{11} - C_{12}$ is computed by determining the slope of the line associated with applying a volume conserving tetragonal strain to the material. $C_{44}$ is computed by determining the slope of the line associated with applying a volume conserving orthorhombic strain to the material.
<table>
<thead>
<tr>
<th>Method</th>
<th>Total</th>
<th>s</th>
<th>p</th>
<th>d</th>
<th>f</th>
</tr>
</thead>
<tbody>
<tr>
<td>LAPW</td>
<td>18.79</td>
<td>0.69</td>
<td>0.75</td>
<td>5.05</td>
<td>5.42</td>
</tr>
<tr>
<td>TB</td>
<td>17.20</td>
<td>0.41</td>
<td>1.89</td>
<td>7.74</td>
<td>7.16</td>
</tr>
</tbody>
</table>

Table 4.6: DOS at the Fermi level for Thorium which shows strong f components. Due to the fact that the decomposed LAPW DOS are projections onto the Muffin-Tin spheres, they do not add up to the total DOS.

Th is $16.95 \text{states/Ry}$; so, our prediction for the electronic specific heat coefficient would be $2.94 \frac{mJ}{\text{moldeg}^2}$. In literature, the measured value for the electronic specific heat coefficient was shown to be $3.44 \frac{mJ}{\text{moldeg}^2}$ which is a bit higher than our prediction; however, we are using zero for the electron-phonon coupling which would account for the majority of the discrepancy.[25] Using a method described by Gaspari and Gyorffy allows the prediction of $\lambda$ from the density of states at the Fermi level and, in this case, would predict $\lambda$ to be $0.34$. [26] Using the predicted value for $\lambda$ produces an electronic specific heat coefficient of $3.97 \frac{mJ}{\text{moldeg}^2}$.

Our predictions for the electronic specific heat coefficient bracket the experimental value. A $\lambda$ value of 0.17 would give agreement with experiment.

### 4.7 Phonons

The experimental phonon information for Thorium was obtained from a 1973 article by Reese, Sinha, and Peterson.[23] During the initial fitting process, several of the phonon values were being computed as negative, specifically for the X coordinate. This error led to a closer examination of the band structure fit and the idea that a direct fit to the full energy bands should be included. After adding the complete band structure to the fit, it was possible to obtain phonon results which reasonably match the experimental results for Thorium. The comparison of our computed phonon frequencies of the experimental values is made in Table 4.7 given the sensitivity of these calculations and the fact that phonons were not included in the fitting database the agreement is good.
(a) Band plot comparison for LAPW and TB results for Thorium. Reasonable agreement is found among most bands except for band 2 between the L and ∆ lines. All eigenvalues have been shifted so that the Fermi level is at zero.

(b) Total DOS plot comparison for LAPW and TB for Thorium. Excellent agreement in the DOS occurs with the locations of the peaks occurring in similar locations. All eigenvalues have been shifted so that the Fermi level is at zero.

(c) Total DOS plot comparison for LAPW and TB for Thorium with the DOS broken down by character.

Figure 4.6: Band plot and DOS comparisons for LAPW and TB results for Thorium
<table>
<thead>
<tr>
<th>Direction</th>
<th>Th - Exp</th>
<th>Th - TB</th>
</tr>
</thead>
<tbody>
<tr>
<td>D1</td>
<td>2.417 THz</td>
<td>2.95 THz</td>
</tr>
<tr>
<td>D5</td>
<td>1.585 THz</td>
<td>1.97 THz</td>
</tr>
<tr>
<td>L2</td>
<td>3.240 THz</td>
<td>2.78 THz</td>
</tr>
<tr>
<td>L3</td>
<td>1.280 THz</td>
<td>1.94 THz</td>
</tr>
<tr>
<td>S1</td>
<td>3.056 THz</td>
<td>3.39 THz</td>
</tr>
<tr>
<td>S2</td>
<td>2.241 THz</td>
<td>1.94 THz</td>
</tr>
<tr>
<td>S3</td>
<td>1.500 THz</td>
<td>2.65 THz</td>
</tr>
<tr>
<td>W2</td>
<td>2.875 THz</td>
<td>2.34 THz</td>
</tr>
<tr>
<td>W5</td>
<td>2.215 THz</td>
<td>3.35 THz</td>
</tr>
<tr>
<td>X3</td>
<td>3.474 THz</td>
<td>2.03 THz</td>
</tr>
<tr>
<td>X5</td>
<td>2.259 THz</td>
<td>3.34 THz</td>
</tr>
</tbody>
</table>

Table 4.7: Thorium phonon frequency comparison of results from paper by Reese, Sinha and Peterson with the TB calculation. All values of the estimated structure are positive and reasonable agreement with experiment is achieved.

<table>
<thead>
<tr>
<th>Vacancy Formation</th>
<th>Th - Exp</th>
<th>Th - TB</th>
</tr>
</thead>
<tbody>
<tr>
<td>124 Atom Cell</td>
<td>0.0354 Ry</td>
<td>-0.0963 Ry</td>
</tr>
<tr>
<td>125 Atom Cell</td>
<td>0.1309 Ry</td>
<td>0.0695 Ry</td>
</tr>
</tbody>
</table>

Table 4.8: Vacancy energy of Thorium. Comparison of the energies of a fully occupied supercell and a supercell with a single atom removed from the origin. The positive vacancy energy indicates that the fully occupied structure is more stable than the structure missing an atom.

### 4.8 Vacancy Formation Energy

The vacancy formation for the FCC structure is tested via an unrelaxed supercell method in which the energy of a cell with a complete lattice is compared to a lattice which has one atom removed (see equation 2.37). Initially, the value of the vacancy formation energy for this calculation was negative for early fits, but the introduction of the band structure to the fitting process helped move the fit to where this value was positive. This value indicates the stability of the structure before the loss of an electron; a positive value means that the structure is more stable in the full lattice configuration. Previous investigation into the vacancy binding energy for Thorium was reported to be 0.0695 Ry.[27] Our value is significantly larger because we have performed an unrelaxed calculation.
4.9 Spin-Orbit Interaction

Following the Podolskiy and Vogl paper we investigated spin-orbit splitting. The spin-orbit parameter values for the d orbital was obtained from Herman and Skilman listings of the atomic values. The value for the d spin-orbit parameter we use is 0.01123 Ry.\cite{28} However, we estimated out spin-orbit parameter for the f-orbital by examining the states at the $\Gamma$ from LAPW calculations including spin orbit effects. We tuned the f spin-orbit parameter to approximate the amount of splitting seen in our LAPW results. The spin-orbit parameter which produced the best agreement with the LAPW spin-orbit data was a value of 0.01 Ry. Figure 4.7 shows a bandplot comparing the TB results with and without spin-orbit splitting. One thing not seen on the graph is that the lower d and f triplets at the $\Gamma$ point become mixed due to the very small gap between those eigenvalues. This is a deviation from the LAPW results which maintain the separation of the lower d and f eigenvalues. The mapping of eigenvalues from the non-spin orbit results to the spin-orbit results at certain high symmetry points is shown in Table 4.9. In general, the spin-orbit effect is small especially for states below the Fermi level that are s or d-like. This means that the total energy results reported here are reliable since the total energy involves mainly the occupied states.

4.10 Conclusion

A complete set of transferable NRL-TB coefficients for Thorium was found that fits very well the LAPW data and has predictive capability for quantities that were not fitted. The current set of coefficients can correctly compute total energy, elastic constants, vacancy formation energy and phonon frequencies which are physically meaningful. Also, during the investigation the importance of fitting to the energy bands as well as the total energy was shown. The addition of a direct fit to the complete band structure at the equilibrium lattice constant helped move the fit from a region in which the vacancy and phonon results were not physically acceptable (e.g. imaginary phonon frequencies). There are minor discrepancies
<table>
<thead>
<tr>
<th>Without Spin</th>
<th>With Spin</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Γ</strong></td>
<td></td>
</tr>
<tr>
<td>-0.3506 (1)</td>
<td>-0.3506 (2)</td>
</tr>
<tr>
<td>0.0411 (1)</td>
<td>0.0396 (2)</td>
</tr>
<tr>
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<tr>
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<tr>
<td>0.5274 (1)</td>
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<tr>
<td><strong>L</strong></td>
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<td></td>
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</tr>
<tr>
<td>0.3256 (1)</td>
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</tbody>
</table>

Table 4.9: Comparison of the eigenvalues for the non-spin-orbit TB program and the TB program implementing the spin-orbit splitting.
Figure 4.7: FCC bands with and without spin-orbit splitting. Both sets of band data are graphed from TB results. Between the energy values of 0.2 Ry and 0.3 Ry, the fine splitting of the bands 3 through 6 can be seen.

In the band structure between the Λ and Δ lines which if addressed would more than likely improve the fit.
Chapter 5: Actinium

5.1 Introduction

This chapter will describe the process by which the modified NRL-TB program was used to find a transferable set of NRL-TB parameters for Actinium. To date, the NRL-TB method has not been applied to Ac. This calculation builds on what was learned during the process of finding the Thorium NRL-TB parameters. The current set of Actinium NRL-TB coefficients only took a few weeks to develop because of improvements made in the process of building and identifying good fits for Th.

5.2 Computational Details

For Actinium, full potential, scalar relativistic LAPW total energy calculations were done using both the GGA and LDA. It turned out that unlike Th the best results with respect to experiment were obtained by the LDA. The LDA was used to form a target database of energies and band structure across a set of lattice constants and lattice types near the theoretical equilibrium volume of Actinium which is an FCC lattice near 10.4 Bohr. Specifically, 6 FCC structures ranging from 9.8 to 10.8 Bohr, 6 BCC structures ranging from 7.6 to 8.6 Bohr, 7 SC structures ranging from 6 to 7.2 Bohr, and 5 diamond structures ranging from 14.1 to 15.5 Bohr. Unlike the Thorium fitting process, it was not necessary to include the elastic constants in the database of the fit.

5.3 Tight-Binding Fit

For the Actinium fit, the total energy RMS error was less than 1 mRy as shown in Table 5.1 and the average band error across 11 bands at the equilibrium lattice location was 18 mRy.
<table>
<thead>
<tr>
<th>Type</th>
<th>Lat Const (Bohr)</th>
<th>LAPW Energy (Ry)</th>
<th>SK Energy (Ry)</th>
<th>Difference (Ry)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FCC</td>
<td>9.8</td>
<td>0.0078</td>
<td>0.0079</td>
<td>0.0001</td>
</tr>
<tr>
<td>FCC</td>
<td>10</td>
<td>0.0028</td>
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</tr>
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<td>FCC</td>
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<td>0.0003</td>
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<tr>
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<td>0.0302</td>
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<td>0.0129</td>
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<td>0</td>
</tr>
<tr>
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<td>0.0697</td>
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</tr>
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<td>0.0509</td>
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</tr>
<tr>
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<td>0.0004</td>
</tr>
<tr>
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<td>0.0597</td>
<td>0</td>
</tr>
<tr>
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</tr>
<tr>
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<td>0.0002</td>
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<td>DIA</td>
<td>15.5</td>
<td>0.1296</td>
<td>0.1295</td>
<td>-0.0001</td>
</tr>
</tbody>
</table>

Table 5.1: Actinium NRL-TB database for the structures and energies fit. The input energies, orthogonal fit energies and the difference between the input and output are shown. The overall energy RMS error of 0.00028 Ry across all structures is excellent.

as shown in Table 5.2. The band errors were a little higher than desired, but the fit did appear to produce good results for most of Actinium’s properties. As with Thorium, the best fit onsite TB coefficients had the additional restriction that the values for $t_{2g}$ and $e_g$ would need to be identical because the crystal field separation of $t_{2g}$ and $e_g$ is only applicable to the cubic symmetry which causes problems for the transferability to other structures. The onsite parameters influence the diagonal elements of the Hamiltonian matrix while the hopping parameters affect the off-diagonal elements. The complete set of onsite and hopping coefficients are shown in Tables 5.3.

The onsite Slater-Koster parameters computed by Equation 3.6 of Section II using the coefficients from Table 5.3 as a function of the FCC lattice constant are plotted in Figure 5.1a. The key feature of this graph is to note that the onsite parameters decrease or
<table>
<thead>
<tr>
<th>Type</th>
<th>Lat Const (Bohr)</th>
<th>Band</th>
<th>RMS Error (Ry)</th>
</tr>
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<td>0.0128</td>
</tr>
<tr>
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<td>2</td>
<td>0.0089</td>
</tr>
<tr>
<td>FCC</td>
<td>10.4</td>
<td>3</td>
<td>0.0127</td>
</tr>
<tr>
<td>FCC</td>
<td>10.4</td>
<td>4</td>
<td>0.0091</td>
</tr>
<tr>
<td>FCC</td>
<td>10.4</td>
<td>5</td>
<td>0.0168</td>
</tr>
<tr>
<td>FCC</td>
<td>10.4</td>
<td>6</td>
<td>0.0215</td>
</tr>
<tr>
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<td>7</td>
<td>0.028</td>
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<tr>
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<td>8</td>
<td>0.0238</td>
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<td>FCC</td>
<td>10.4</td>
<td>9</td>
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<tr>
<td>FCC</td>
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<td>11</td>
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<tr>
<td></td>
<td>Average RMS</td>
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<td>0.0181</td>
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</table>

Table 5.2: Actinium Band fit at the FCC equilibrium lattice constant 10.4. Since each band has 85 points only the RMS error across all k-points in a band is shown. The overall energy RMS error of 0.018077 is acceptable.

### Best Fit Parameters - Actinium

<table>
<thead>
<tr>
<th>λ</th>
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<tr>
<td>On-site</td>
<td>a</td>
</tr>
<tr>
<td>s</td>
<td>-0.05555</td>
</tr>
<tr>
<td>p</td>
<td>0.19592</td>
</tr>
<tr>
<td>t2g / eg</td>
<td>0.17455</td>
</tr>
<tr>
<td>f</td>
<td>0.49724</td>
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<tr>
<td>Hopping</td>
<td>e</td>
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<tr>
<td>ssσ</td>
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</tr>
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<td>spσ</td>
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<tr>
<td>ppσ</td>
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<tr>
<td>ppτ</td>
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<tr>
<td>pdτ</td>
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<tr>
<td>ddσ</td>
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<td>ddτ</td>
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<td>pdτ</td>
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<tr>
<td>ddτ</td>
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<td>pdσ</td>
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<tr>
<td>pdτ</td>
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<tr>
<td>ddδ</td>
<td>218.29982</td>
</tr>
<tr>
<td>dfσ</td>
<td>-182.50301</td>
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</table>

Table 5.3: The best fit Actinium coefficients. Since for the cubic structure t_{2g} and e_{g} we set to equal each other, only a single set of coefficients is computed for t_{2g} and e_{g}.
Figure 5.1: Onsite and Hopping integral graphs for Actinium. In the onsite graph shows that the f orbitals contribute significantly to the overall Hamiltonian. The two-center hopping integrals show all the energies asymptotically approaching zero.

remain stable as the the lattice constant increases, except the f-onsite parameter which is relatively invariant to the lattice size and appears to become the major contributor to the Hamiltonian at larger lattice constants. Selected hopping Slater-Koster parameters computed by Equation 3.9 of Section II using the coefficients from Table 5.3 as a function of the distance R are shown in Figure 5.1b. All the functions asymptotically approaching zero, but the fact that some of the lines cross zero (e.g. $ff\pi$) could warrant further investigation.

5.4 Ground-State Behavior and Phase Stability

Given the coefficients listed in Table 5.3, the NRL static program was used to examine the different lattice structures as shown in Figure 5.2. The value of determining a set of transferable fitting coefficients is seen in this example. For the same set of coefficients a variety of structures can be examined, ones which were fit (e.g. FCC, BCC, SC, DIA) and structures which were not fit (e.g. HCP, L12, and A15). It should be noted that before computing the fit for HCP, a side analysis of how HCP energy varied for different c/a ratios to determine the c/a ratio which would produce the lowest HCP energies. That analysis showed that a c/a ratio of 1.60 would produce the most stable configurations. A graph showing FCC compared to HCP at some c/a ratios at and near the equilibrium c/a for
Figure 5.2: Energy-volume behavior of Actinium across several different structures. All curves show a local minimum and are well behaved in the region plotted. In particular, FCC is seen to be the most stable structure since it has the minimum energy across all structures.

Thorium is shown in Figure 5.3. The L12 structure is similar to the AuCu3 structure and normally has four atoms in the unit cell; however, for the L12 structure the Au atom at the origin is removed. The positions for the other three atoms are at (0.00, 0.50, 0.50), (0.50, 0.00, 0.50), and (0.50, 0.50, 0.50). The A15 structure is also known as Cr3Si and has eight atoms in the unit cell. The positions for the eight atoms are (0.00, 0.00, 0.00), (0.50, 0.50, 0.50), (0.25, 0.50, 0.00), (0.75, 0.50, 0.00), (0.00, 0.25, 0.50), (0.00, 0.75, 0.50), (0.50, 0.00, 0.25), and (0.50, 0.00, 0.75). Computing a quadratic fit or birch fit to the static data, the minimum energy and corresponding lattice constant for each type of structure can be found. A summary of those minimum energy values and volumes and how they compared to the LAPW data is shown in Table 5.4.

Another investigation into the stability of the fit would be to examine structures of lower symmetry. The Bain path, shown in Figure 5.4, shows the energy of Actinium under a volume conserving tetragonal strain. The curve properly shows that at the FCC structure
Figure 5.3: The graphs show the Actinium HCP investigation to find the best c/a ratio to compute the HCP energies. The minimum energy for the HCP structure was found for a c/a ratio of 1.60 for the HCP volume 580.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Ac LAPW</th>
<th>Ac TB</th>
</tr>
</thead>
<tbody>
<tr>
<td>SC</td>
<td>0.0492 Ry 6.81 Bohr</td>
<td>0.051 Ry 6.79 Bohr</td>
</tr>
<tr>
<td>BCC</td>
<td>0.0096 Ry 8.28 Bohr</td>
<td>0.010 Ry 8.30 Bohr</td>
</tr>
<tr>
<td>FCC</td>
<td>0.0000 Ry 10.40 Bohr</td>
<td>0.000 Ry 10.34 Bohr</td>
</tr>
<tr>
<td>DIA</td>
<td>-</td>
<td>0.125 Ry 14.79 Bohr</td>
</tr>
<tr>
<td>HCP</td>
<td>-</td>
<td>0.001 Ry c = 11.90 Bohr c/a = 1.60</td>
</tr>
<tr>
<td>A15</td>
<td>-</td>
<td>0.008 Ry 6.75 Bohr</td>
</tr>
<tr>
<td>L12</td>
<td>-</td>
<td>0.045 Ry 6.46 Bohr</td>
</tr>
</tbody>
</table>

Table 5.4: Comparison of LAPW and fit structure energies and volumes for Actinium. The c/a ratio for HCP was used since it would produce the minimum HCP energy across all c/a values. FCC is shown to be the most stable structure since it has the lowest energy.
Figure 5.4: Tight-binding calculation of the energy of Actinium under a tetragonal strain (the Bain Path) as a function of c/a. The vertical lines denote the positions for the BCC and FCC lattices.

Table 5.5: Elastic constants for Actinium. The fact that all three elastic constants have positive values indicates that fcc structure is mechanically stable.

<table>
<thead>
<tr>
<th>Actinium</th>
<th>Experimental</th>
<th>LAPW</th>
<th>TB Ortho</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk</td>
<td>-</td>
<td>25.99 GPa</td>
<td>25.88 GPa</td>
</tr>
<tr>
<td>$C_{11} - C_{12}$</td>
<td>-</td>
<td>38.90 GPa</td>
<td>23.00 GPa</td>
</tr>
<tr>
<td>$C_{44}$</td>
<td>-</td>
<td>22.94 GPa</td>
<td>22.68 GPa</td>
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</tbody>
</table>

5.5 Elastic Constants

The elastic constants were computed as a by product of the Birch fit and by applying the appropriate volume conserving tetragonal or orthorhombic strains to the lattice. All three values, B, $C_{11} - C_{12}$, and $C_{44}$ are positive values indicating the fcc structure is mechanically stable. There currently are no experimental values to compare against.
Figure 5.5: Energy graphs for determining the elastic constants of Actinium. The Bulk Modulus is determined by computing the partial derivative of the change in energy per volume. $C_{11} - C_{12}$ is computed by determining the slope of the line associated with applying a volume conserving tetragonal strain to the material. $C_{44}$ is computed by determining the slope of the line associated with applying a volume conserving orthorhombic strain to the material.
Table 5.6: DOS at the Fermi level for Actinium which does not have a strong f components. Due to fact that the decomposed LAPW DOS are projections onto the Muffin-Tin spheres, they do not add up to the total DOS.

<table>
<thead>
<tr>
<th>Method</th>
<th>Total</th>
<th>s</th>
<th>p</th>
<th>d</th>
<th>f</th>
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</thead>
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<td>LAPW</td>
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<td>TB</td>
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<td>2.19</td>
<td>14.99</td>
<td>3.29</td>
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</tbody>
</table>

5.6 Electronic Structure

Both the TB bands and the density of states (DOS) match the related LAPW data for the FCC structure at equilibrium as shown in Figure 5.6a. This verifies the quality of the fit. In Figure 5.6a, we note that the occupied TB bands match the LAPW bands well across all bands. We also see that the f-bands are above the Fermi level as would be expected. The best fits for the bands are for the lower 4 bands which encompass most of the occupied states. The fit for the upper bands is where the majority of the error is occurring. In the DOS plot, we do not see as sharply peaked values, but the overall trend of the graphs match. As with Th, we will look for the placement of the Γ_{2'} band. This band is the first to have any significant f-character; however, we can see that the Γ_{2'} band is completely above the Fermi level. The fact that there was little f-orbital interaction at the Fermi level may explain why fitting Ac was easier than Th. Using the DOS at the Fermi level and assuming that electron-phonon coupling, λ, is zero, an estimation for the electronic specific heat coefficient can be made using Equation 2.34. At the Fermi level, the DOS for Ac is 20.80; so, our prediction for the electronic specific heat coefficient would be 3.61 \( \frac{mL}{mol\text{deg}^2} \). There are not experimental results available with which to compare our predicted value.

5.7 Phonons

Although there were not specific experimental results to compare, the phonon results show no anomalies such as negative frequencies. If more phonon locations were computed, it could be determine which axis allow for favorable passage of phonon waves. During the
(a) Band plot comparison for LAPW and TB results for Actinium. All eigenvalues have been shifted so that the Fermi level is at zero.

(b) Total DOS plot comparison for LAPW and TB for Actinium. The general trend of the DOS is follow, but some of the sharper peaks are not reproduced. All eigenvalues have been shifted so that the Fermi level is at zero.

(c) Total DOS plot comparison for LAPW and TB for Actinium with the DOS broken down by character.

Figure 5.6: Band plot and DOS comparisons for LAPW and TB results for Actinium
Table 5.7: Actinium phonon results. All values of the estimated structure are positive showing that they may be physically possible.

<table>
<thead>
<tr>
<th></th>
<th>Direction</th>
<th>Ac - TB</th>
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<tr>
<td>D1</td>
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<tr>
<td>D5</td>
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</tr>
<tr>
<td>L2</td>
<td>Longitudinal</td>
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</tr>
<tr>
<td>L3</td>
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<tr>
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<td>Longitudinal</td>
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</tr>
<tr>
<td>S2</td>
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<tr>
<td>S3</td>
<td>Transverse</td>
<td>1.35 THz</td>
</tr>
<tr>
<td>W2</td>
<td>Π</td>
<td>1.83 THz</td>
</tr>
<tr>
<td>W5</td>
<td>Λ</td>
<td>1.58 THz</td>
</tr>
<tr>
<td>X3</td>
<td>Longitudinal</td>
<td>2.35 THz</td>
</tr>
<tr>
<td>X5</td>
<td>Transverse</td>
<td>1.84 THz</td>
</tr>
</tbody>
</table>

Table 5.8: Vacancy energy of Actinium. Comparison of the energies of a fully occupied supercell and a supercell with a single atom removed from the origin. The positive vacancy energy indicates that the fully occupied structure is more stable than the structure missing an atom.

<table>
<thead>
<tr>
<th></th>
<th>124 Atom Cell</th>
<th>125 Atom Cell</th>
<th>Vacancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Actinium</td>
<td>0.592 Ry</td>
<td>0.468 Ry</td>
<td>0.124 Ry</td>
</tr>
</tbody>
</table>

fitting process for Actinium, the base database information of energy and band data did not include phonon data. The predicted phonon values for Actinium are shown in Table 5.7.

5.8 Vacancy Formation

The vacancy formation for the FCC structure is tested via an unrelaxed supercell method in which the energy of a cell with a complete lattice is compared to a lattice which has one atom removed (see equation 2.37). Like the phonon results, no vacancy information was included in the fit. The vacancy formation energy indicates the stability of the structure due to the loss of an atom; a positive value means that the structure is more stable in the full lattice configuration.

Because the f-states for Actinium are high above the Fermi level, it was possible to attempt a fit of Actinium to produce a set of best fit spd coefficients which could be used
in the existing NRL Molecular Dynamics (NRL-MD) code. The NRL-MD code will allow
the computation of the mean square displacement (MSD) of the atoms in the lattice vs.
temperature and both unrelaxed and relaxed vacancy formation energies. The best fit spd
coefficients are listed in Appendix B. The best fit spd coefficients produces a MSD which
increases almost linearly with temperature as shown in Figure 5.7. The comparison of the
original spdf unrelaxed vacancy formation energy with the unrelaxed and relaxed spd MD
calculations is shown in Table 5.9. The results between the spdf TB and spd MD unrelaxed
calculations are in reasonably good agreement.

Figure 5.7: MD mean square displacements (MSD) for Actinium as a function of tempera-
ture.

<table>
<thead>
<tr>
<th></th>
<th>Comparison Vacancy Formation Energies (Ac)</th>
</tr>
</thead>
<tbody>
<tr>
<td>spdf TB (unrelaxed)</td>
<td>0.124 Ry</td>
</tr>
<tr>
<td>spd MD (unrelaxed)</td>
<td>0.096 Ry</td>
</tr>
<tr>
<td>spd MD (relaxed)</td>
<td>0.048 Ry</td>
</tr>
</tbody>
</table>

Table 5.9: Comparison of spdf TB (unrelaxed) calculations to spd MD (unrelaxed) and spd
MD (relaxed) calculations.
5.9 Conclusion

The modified NRL-TB program was able to produce a set of transferable coefficients which was able to predict values for lattice constants and structures for locations which were fit and ones which were not fit. The error in the band fit was mostly contributed by the bands which were above the Fermi level. Considering that the convergence of a set of best fit coefficients which produced physically realizable results across all of our tests so quickly, it might be better to concentrate more on fitting the lower occupied states than the states which lie well above the Fermi level.
Chapter 6: Summary and Future Work

6.1 Summary

The current expansion of the NRL-TB program is now able to generate transferable sets of coefficients for both Thorium and Actinium. The current research analysis could be improved in two ways in the near future. One avenue of research would be to complete the investigation of finding fitting coefficients for the rest of the Lanthanides and Actinides. A second avenue of research would be add the current modification to NRL’s Molecular Dynamics code. The NRL-MD package provides capabilities not available in the static or fitting programs which were modified.

6.2 Molecular Dynamics Expansion

Both the fitting code and the static code which were modified are designed to only examine systems where the atoms in the system are stationary. The molecular dynamics code allows the system of atoms to move in time. By examining the averages of the physical properties in time a different perspective on how the material will behave can be examined. Specifically, periodic properties, such as phonons, may be better explored through molecular dynamic simulations than through static computation of values. The update to the NRL-MD code would allow for the proper calculation of the forces and energies at the individual steps in the simulation.

6.3 Conclusion

The NRL-TB program was successfully expanded to include the effects of f-orbital electrons and with this expanded application it was possible to fit the primary properties of Thorium
and Actinium, materials whose properties are dependent on the f-orbitals, and find a set of transferable coefficients which allowed the investigation of both the structures fit and structures which were not fit. During the fitting process, the flexibility of the NRL-TB program allowed fitting to not only first-principles results but also to estimates for desired results (e.g. elastic constants) so that a good fit could be found. Although not fully explored in this paper, the process of adding desired results and modifying first-principles results to what is fit could result in producing NRL-TB parameters which could correct for differences between first-principles results and experiment. The improvements and insights found during the yearlong investigation of Thorium, enabled the investigation of Actinium only to take several weeks.

The NRL-TB program can also be run in a non-orthogonal mode. This additional fitting investigation should be done to see if a non-orthogonal fit which is better than the current orthogonal fit can be found. Also, the same changes which were used to expand the tbfit and static programs should be added to the NRL’s molecular dynamics application. Lastly, now that the fitting process has been expanded and tested, other f orbital dependent materials within the lanthanides and actinides can be investigated.
Appendix A: Developed Computer Code

The majority of the new code which was added is contained in the rotate\_new.f file which were used to expand the fitting and static code. The rotate\_new.f for file for the fitting code is slightly different than the rotate\_new.f. The primary difference between the two codes is that an additional change was made to the fitting code to improve speed. This speed improvement was not added to the static code because in the static case the matrices could not be redimensioned to handle the number of atoms that occur during supercell calculations.

Only some small additional changes in both the fitting and static code needed to be made to the existing files to take advantage of the new code. This is a summary for how the other files needed to be modified.

- rotate v4.f : contains all new routines.
- search2.f : call SETUP QARRAY to set the (l,m) values for use during the computation of the integral coefficients and HF2 to compute the integral coefficients
- skgen v4.f and func v4.f : call SETUP SK LATTICE INTEGRALS which fills in the matrix which contains the integral values
- setup v4.f : additional calculation of f onsite contribution and f hopping contributions to Hamiltonian
- rotate.f : needed to have matrices expanded from 9x9 to 16x16 and modified computation of Hamiltonian elements to loop of the orbital contributions
- symmeg.f : change appropriate symmetry calculations and added additional symmetry calculations

A schematic of where the changes fit within the NRL-TB calculation process is shown in Figure A.1.
Figure A.1: Schematic of where the modifications to the code fit within NRL-TB calculation process.
A.1 rotate_new.f Code for Fitting

SUBROUTINE SETUP_QARRAY()

! IMPLICIT NONE

INCLUDE 'global_vars.txt'

gQArray(1,1) = 0
gQArray(1,2) = 0
gQArray(2,1) = 1
gQArray(2,2) = 1
gQArray(3,1) = 1
gQArray(3,2) = -1
gQArray(4,1) = 1
gQArray(4,2) = 0
gQArray(5,1) = 2
gQArray(5,2) = -1
gQArray(6,1) = 2
gQArray(6,2) = 1
gQArray(7,1) = 2
gQArray(7,2) = -2
gQArray(8,1) = 2
gQArray(8,2) = 2
gQArray(9,1) = 2
gQArray(9,2) = 0
gQArray(10,1) = 3
gQArray(10,2) = 0
gQArray(11,1) = 3
gQArray(11,2) = 1
gQArray(12,1) = 3
gQArray(12,2) = -1
gQArray(13,1) = 3
gQArray(13,2) = 2
gQArray(14,1) = 3
gQArray(14,2) = -2
gQArray(15,1) = 3
gQArray(15,2) = 3
gQArray(16,1) = 3
gQArray(16,2) = -3

END SUBROUTINE SETUP_QARRAY
END

SUBROUTINE SETUP_SK_LATTICE_INTEGRALS(inS, param)
IMPLICIT REAL*8 (A-H,O-Z)
!
USE GLOBAL_VARIABLES
!
IMPLICIT NONE
!
INCLUDE 'global_vars.txt'
include 'P1'
common /pairs/tt_list(3,mpair,nstrucd),
$ dlv_list(3,mpair,nstrucd),dist_list(mpair,nstrucd),
$ screen_list(mpair,nstrucd),jkind_list(mpair,2,nstrucd),
$ jatm_list(mpair,2,nstrucd),npairs(nstrucd)
common/latt1/plv(3,3,nstrucd),dnnsq(mkind,mkind,mnn),
$ den(mkind,matom,nstrucd),dnn(mkind,mkind,mnn)
dimension param(npard)
INTEGER inS
INTEGER ipair
DOUBLE PRECISION TotalDensity, EffDensity
DOUBLE PRECISION dist
double PRECISION dLambda
double PRECISION dLNRad
double PRECISION dLNCut
INTEGER isK, isKIndex, isKIndex2

TotalDensity = 0.0d0
do ipair = 1, npairs(inS)
    dist=dist_list(ipair, inS)
dLambda= param(1)
dLNRad = dist_list(ipair, inS)
dLNCut = screen_list(ipair, inS)
    EffDensity = dLNCut * Exp(-(dLambda**2d0) * dLNRad)
    TotalDensity = TotalDensity + EffDensity
do iSK = 1, 40
    isKIndex = 3*(iSK-1)+22
    isKIndex2 = (iSK-1)+142
    dE = param(isKIndex)
    dF = param(isKIndex+1)
    dG = param(isKIndex+2)
    dH = param(isKIndex2)
    gSKValues(isK,ipair)=((dE+(dF*dLNRad)+(dG*(dLNRad**2.0d0)))*$
    exp(-dLNRad*(dH**2.0d0)))*dLNCut
end do
end do

C den(jkind(2),iat,inS)=den(jkind(2),iat,jstruc)+dent
den(1,1,inS)=TotalDensity

do j = 1, 5
    iSKIndex = 4*(j-1) + 2
    dA = param(iSKIndex)
    dB = param(iSKIndex + 1)
    dC = param(iSKIndex + 2)
    dD = param(iSKIndex + 3)
    gSKOnsite(j) = dA+(dB*(TotalDensity**(2.d0/3.d0)))+
$       (dC*(TotalDensity**(4.d0/3.d0)))+ (dD*(TotalDensity**2.d0))
$ end do 

C Prepare for main matrix values

do ipair = 1, npairs(inS)
    do iI = 1, 16
        do iJ = 1, 16
            aFactor = 0
            do j = 1, gSKCoeffsNZC(inS,ipair,iI,iJ)
                iCI = gSKCoeffsNZI(inS,ipair,iI,iJ,j)
                aFactor = aFactor + gSKCoeffs(inS,ipair,iI,iJ,iCI)
$                * gSKValues(iCI,ipair)
            end do
            gSKIntegrals(ipair, iI, iJ) = aFactor
        end do
    end do
end do

C Prepare for main overlap values

do ipair = 1, npairs(inS)
! END SUBROUTINE SETUP_SK_LATTICE_INTEGRALS

DOUBLE PRECISION FUNCTION FACT(inVal)

! IMPLICIT NONE

INTEGER inVal
INTEGER iReturn
INTEGER i

iReturn = 1
DO i = 1, inVal
   iReturn = iReturn * i
END DO
FACT = iReturn

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DOUBLE PRECISION FUNCTION BINOMIAL(n, k)
!
  IMPLICIT NONE

INTEGER n
INTEGER k
DOUBLE PRECISION FACT

BINOMIAL = FACT(n)/((FACT(n-k)*FACT(k)))
!
END FUNCTION BINOMIAL
END

DOUBLE PRECISION FUNCTION d(l, m, mp)
!
  USE GLOBAL_VARIABLES
!
  IMPLICIT NONE

INCLUDE 'global_vars.txt'

INTEGER l
INTEGER m
INTEGER mp
DOUBLE PRECISION prefR
DOUBLE PRECISION summ
DOUBLE PRECISION dPart
INTEGER lt

DOUBLE PRECISION FACT
prefR=(FACT(l+mp)*FACT(l-mp)*FACT(l+m)*FACT(l-m))

IF (prefR .GT. 0) THEN
    prefR = (2.0**(-l))*(prefR**(0.5))
END IF

summ = 0.0
DO lt = 0, (2*l+1)
    IF ((l+mp-lt) .GE. 0) THEN
        IF ((l-m-lt) .GE. 0) THEN
            IF ((lt+m-mp) .GE. 0) THEN
                dPart = ((-1.0)**lt)
                dPart = dPart/(FACT(l+mp-lt)*FACT(l-m-lt)*FACT(lt)*FACT(lt+m-mp))
                dPart = dPart * ((1-gN)**(lt+((m-mp)/2.0)))
                summ = summ + dPart*(((1+gN)**(l-lt-((m-mp)/2.0))))
            END IF
        END IF
    END IF
END DO

END DO

END IF
END IF
END IF
END IF
END DO

d = prefR*summ

END FUNCTION d

END

DOUBLE PRECISION FUNCTION DTAU(m)

!  IMPLICIT NONE

INTEGER m
IF (m .GE. 0) THEN
   DTAU = 1.0
ELSE
   DTAU = 0.0
END IF

! END FUNCTION DTAU

END

DOUBLE PRECISION FUNCTION CC(m)

! IMPLICIT NONE
INCLUDE 'global_vars.txt'

INTEGER m
DOUBLE PRECISION sumc
DOUBLE PRECISION dPart1
INTEGER k
DOUBLE PRECISION BINOMIAL

sumc = 0.0
DO k = 0, Int(m/2)
   dPart1 = ((-1.0)**k)*BINOMIAL(m,2*k)
   dPart1 = dPart1*((-gL/((1.0-gN**2.0)**0.5))**(m-2.0*k))
   dPart1 = dPart1*(((gM)/((1.0-gN**2.0)**0.5))**(2.0*k))
   sumc = sumc + dPart1
END DO

CC = sumc

! END FUNCTION CC

END
DOUBLE PRECISION FUNCTION SS(m)

! USE GLOBAL_VARIABLES
! IMPLICIT NONE

INCLUDE 'global_vars.txt'

INTEGER m
DOUBLE PRECISION sumc
dDOUBLE PRECISION dPart1
INTEGER k
DOUBLE PRECISION BINOMIAL

sumc = 0.0
DO k = 0, Int((m-1)/2)
    dPart1 = ((-1.0)**k)*BINOMIAL(m,(2*k)+1)
    dPart1 = dPart1*((-gL/((1.0-gN**2.0)**0.5))**(m-2.0*k-1.0))
    dPart1 = dPart1*(((gM)/((1.0-gN**2.0)**0.5))**(2.0*k+1.0))
    sumc = sumc + dPart1
END DO
SS = sumc

! END FUNCTION SS
END

DOUBLE PRECISION FUNCTION A(m)

! USE GLOBAL_VARIABLES
! IMPLICIT NONE

INCLUDE 'global_vars.txt'

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INTEGER m

DOUBLE PRECISION DTAU, CC, SS

IF (m .eq. 0) THEN
   A = 1.0D0 / (2.0D0**0.5D0)
ELSE
   ! A=((-1.0)**Abs(m))*(DTAU(m)*CC(Abs(m))-DTAU(-m)*SS(Abs(m)))
   A = ((-1.0)**Abs(m))*(DTAU(m)*Cos(Abs(m)*gGamma)-DTAU(-m)*Sin(Abs(m)*gGamma))
END IF
! END FUNCTION A

END

DOUBLE PRECISION FUNCTION B(m)

! USE GLOBAL_VARIABLES
! IMPLICIT NONE
! INCLUDE 'global_vars.txt'

INTEGER m

DOUBLE PRECISION DTAU, CC, SS

If (m .EQ. 0) Then
   B = 0.0
ELSE
   ! B =((-1.0)**Abs(m))*(DTAU(m)*SS(Abs(m)))+DTAU(-m)*CC(Abs(m)))
   B = ((-1.0)**Abs(m))*(DTAU(m)*Sin(Abs(m)*gGamma)+DTAU(-m)*Cos(Abs(m)*gGamma))
END IF
DOUBLE PRECISION FUNCTION S(l, m, mp)

! USE GLOBAL_VARIABLES
!
! IMPLICIT NONE
!
! INCLUDE 'global_vars.txt'

INTEGER l, m, mp
DOUBLE PRECISION d, A

S = A(m) * ((-1.0)**Abs(mp)) * d(l, Abs(m), Abs(mp)) +
   & d(l, Abs(m), -Abs(mp))

! END FUNCTION S

END

DOUBLE PRECISION FUNCTION T(l, m, mp)

! USE GLOBAL_VARIABLES
!
! IMPLICIT NONE
!
! INCLUDE 'global_vars.txt'

INTEGER l, m, mp
DOUBLE PRECISION d, B

IF (m .EQ. 0) THEN
   T = 0.0
ELSE
INTEGER FUNCTION MAT2(l, m, n)

! USE GLOBAL_VARIABLES

! IMPLICIT NONE

INCLUDE 'global_vars.txt'

INTEGER l, m, n

INTEGER matIndex

INTEGER i, j, k

matIndex = 0
DO i = 0, m-1
  DO j = 0, i
    DO k = 0, j
      matIndex = matIndex + 1
    END DO
  END DO
END DO

DO i = 0, l-1
  DO j = 0, i
    matIndex = matIndex + 1
  END DO
END DO

END FUNCTION MAT2
matIndex = matIndex + n + 1

MAT2 = matIndex

! END FUNCTION MAT2
END

SUBROUTINE HF2(l1, m1, l2, m2, iS, iA, iR, iC)
! USE GLOBAL_VARIABLES
! IMPLICIT NONE
! INCLUDE 'global_vars.txt'

INTEGER l1, m1, l2, m2
INTEGER iS, iA, iR, iC

INTEGER mp
DOUBLE PRECISION sumt
DOUBLE PRECISION dDistance

DOUBLE PRECISION d, S, T, A
INTEGER iM, MAT2

IF (gL .EQ. 0) THEN
  IF (gM .GE. 0) THEN
    gGamma = 3.14159 / 2.0
  ELSE
    gGamma = 3.0*3.14159/2.0
  END IF
ENDIF
ELSE
    gGamma = ATAN2(gM, -gL)
END IF

sumt = 0.0

DO mp = 1, MIN(l1, l2)
    iM = MAT2(Min(l1, l2), Max(l1, l2), Abs(mp))
    gSKCoeffs(iS,iA,iR,iC,iM) = gSKCoeffs(iS,iA,iR,iC,iM) +
    &   (S(l1, m1, mp)*S(l2, m2, mp) + T(l1, m1, mp)*T(l2, m2, mp))
END DO

iM = MAT2(Min(l1, l2), Max(l1, l2), 0)

sumt = (S(l1, m1, mp)*S(l2, m2, mp) + T(l1, m1, mp)*T(l2, m2, mp))

DO mp = 1, 20
    gSKCoeffs(iS,iA,iR,iC,mp) = sumt*gSKCoeffs(iS,iA,iR,iC,mp)
END DO

! END SUBROUTINE HF2
END

A.2 rotate_new.f Code for Static

SUBROUTINE SETUP_QARRAY()
    ! IMPLICIT NONE
    INCLUDE 'global_vars.txt'

    gQArray(1,1) = 0
    gQArray(1,2) = 0
    gQArray(2,1) = 1

END
gQArray(2,2) = 1

gQArray(3,1) = 1

gQArray(3,2) = -1

gQArray(4,1) = 1

gQArray(4,2) = 0

gQArray(5,1) = 2

gQArray(5,2) = -1

gQArray(6,1) = 2

gQArray(6,2) = 1

gQArray(7,1) = 2

gQArray(7,2) = -2

gQArray(8,1) = 2

gQArray(8,2) = 2

gQArray(9,1) = 2

gQArray(9,2) = 0

gQArray(10,1) = 3

gQArray(10,2) = 0

gQArray(11,1) = 3

gQArray(11,2) = 1

gQArray(12,1) = 3

gQArray(12,2) = -1

gQArray(13,1) = 3

gQArray(13,2) = 2

gQArray(14,1) = 3

gQArray(14,2) = -2

gQArray(15,1) = 3

gQArray(15,2) = 3

gQArray(16,1) = 3

gQArray(16,2) = -3

! END SUBROUTINE SETUP_QARRAY
END

SUBROUTINE SETUP_QARRAY_NEW()
!
IMPLICIT NONE
!
INCLUDE 'global_vars.txt'


gQArray(1,1) = 0
gQArray(1,2) = 0
gQArray(2,1) = 1
gQArray(2,2) = 1
gQArray(3,1) = 1
gQArray(3,2) = -1
gQArray(4,1) = 1
gQArray(4,2) = 0
gQArray(5,1) = 2
gQArray(5,2) = -1
gQArray(6,1) = 2
gQArray(6,2) = 1
gQArray(7,1) = 2
gQArray(7,2) = -2
gQArray(8,1) = 2
gQArray(8,2) = 2
gQArray(9,1) = 2
gQArray(9,2) = 0
gQArray(10,1) = 3
gQArray(10,2) = -1

gQArray(11,1) = 3

! END SUBROUTINE SETUP_QARRAY

END

SUBROUTINE COMPUTE_LATTICE_COMPONENT(inR, inC, outRes)

! USE GLOBAL_VARIABLES

! IMPLICIT NONE

INCLUDE 'global_vars.txt'

INTEGER inIndex

INTEGER inR, inC

COMPLEX*16 outRes

DOUBLE PRECISION inL, inM, inN

INTEGER inType

COMPLEX*16 aFactor, aMultiplier
DOUBLE PRECISION dIntegral, dDenominator, dKdotR

DOUBLE PRECISION HF

dIntegral = HF(gQArray(inR, 1), gQArray(inR, 2),
&   gQArray(inC, 1), gQArray(inC, 2))

C WRITE(*,*) "int : ", dIntegral

aMultiplier = DCMPLX(dIntegral, 0.0D0)

! dKdotR = (gL*gXX + gM*gYY + gN*gZZ) * (3.14159D0 / 4.D0)
! aFactor = DCMPLX(COS(dKdotR), SIN(dKdotR))
! outRes = aMultiplier*aFactor
outRes = aMultiplier

! END SUBROUTINE COMPUTE_LATTICE_COMPONENT

END


! USE GLOBAL_VARIABLES
! IMPLICIT NONE
INCLUDE 'global_vars.txt'

INTEGER inS, inA, inR, inC
COMPLEX*16 outRes

COMPLEX*16 aMultiplier

DOUBLE PRECISION dIntegral

dIntegral = 0.0D0
DO I = 1,20
dIntegral=dIntegral
& + gSKCoeffs(inS,inA,inR,inC,I)*gSKFactors(I)
END DO
aMultiplier = DCMPLX(dIntegral, 0.0D0)
outRes = aMultiplier
C WRITE(92,"(3i,f10.5)") inA, inR, inC, dIntegral
! END SUBROUTINE COMPUTE_LATTICE_COMPONENT2
END

DOUBLE PRECISION FUNCTION FACT(inVal)
!
IMPLICIT NONE

INTEGER inVal
INTEGER iReturn
INTEGER i

iReturn = 1
DO i = 1, inVal
   iReturn = iReturn * i
END DO
FACT = iReturn
!
END FUNCTION FACT
END

DOUBLE PRECISION FUNCTION BINOMIAL(n, k)
!
IMPLICIT NONE

INTEGER n
INTEGER k
DOUBLE PRECISION FACT

BINOMIAL = FACT(n)/((FACT(n-k)*FACT(k)))

! END FUNCTION BINOMIAL

END

DOUBLE PRECISION FUNCTION d(l, m, mp)

! USE GLOBAL_VARIABLES
! IMPLICIT NONE
INCLUDE 'global_vars.txt'

INTEGER l
INTEGER m
INTEGER mp
DOUBLE PRECISION prefR
DOUBLE PRECISION summ
DOUBLE PRECISION dPart
INTEGER lt

DOUBLE PRECISION FACT

prefR=(FACT(l+mp)*FACT(l-mp)*FACT(l+m)*FACT(l-m))

IF (prefR .GT. 0) THEN
    prefR = (2.0**(-l))*(prefR**0.5)
END IF
SUMM = 0.0
DO LT = 0, (2*L+1)
  IF ((1+MP-LT) .GE. 0) THEN
    IF ((1-M-LT) .GE. 0) THEN
      IF ((LT+M-MP) .GE. 0) THEN
        DPART = ((-1.0)**LT)
        DPART = DPART/(FACT(1+MP-LT)*FACT(1-M-
                       & LT)*FACT(LT)*FACT(LT+M-MP))
        DPART = DPART * ((1-gN)**(LT+(M-MP)/2.0))
        SUMM = SUMM + DPART*((1+Gn)**(1-LT-(M-MP)/2.0))
      END IF
    END IF
  END IF
END DO
D = PREFR*SUMM
! END FUNCTION D

END

DOUBLE PRECISION FUNCTION DTAU(M)
!
  IMPLICIT NONE

  INTEGER M

  IF (M .GE. 0) THEN
    DTAU = 1.0
  ELSE
    DTAU = 0.0
  END IF

END
DOUBLE PRECISION FUNCTION CC(m)

! IMPLICIT NONE

INCLUDE 'global_vars.txt'

INTEGER m
DOUBLE PRECISION sumc
DOUBLE PRECISION dPart1
INTEGER k
DOUBLE PRECISION BINOMIAL

sumc = 0.0
DO k = 0, Int(m/2)
   dPart1 = ((-1.0)**k)*BINOMIAL(m,2*k)
   dPart1 = dPart1*((-gL/((1.0-gN**2.0)**0.5))**(m-2.0*k))
   dPart1 = dPart1*(((gM)/((1.0-gN**2.0)**0.5))**(2.0*k))
   sumc = sumc + dPart1
END DO
CC = sumc

! END FUNCTION CC

DOUBLE PRECISION FUNCTION SS(m)

! USE GLOBAL_VARIABLES
! IMPLICIT NONE

INCLUDE 'global_vars.txt'
INTEGER m
DOUBLE PRECISION sumc
DOUBLE PRECISION dPart1
INTEGER k
DOUBLE PRECISION BINOMIAL

sumc = 0.0
DO k = 0, Int((m-1)/2)
   dPart1 = ((-1.0)**k)*BINOMIAL(m,(2*k)+1)
   dPart1 = dPart1*((-gL/((1.0-gN**2.0)**0.5))**(m-2.0*k-1.0))
   dPart1 = dPart1*(((gM)/((1.0-gN**2.0)**0.5))**(2.0*k+1.0))
   sumc = sumc + dPart1
END DO
SS = sumc
!   END FUNCTION SS
END

DOUBLE PRECISION FUNCTION A(m)
!   USE GLOBAL_VARIABLES
!   IMPLICIT NONE
   INCLUDE 'global_vars.txt'

INTEGER m
DOUBLE PRECISION DTAU, CC, SS

IF (m .eq. 0) THEN
   A = 1.0D0 / (2.0D0**0.5D0)
ENDIF
ELSE
    !
    A = ((-1.0)**Abs(m))*(DTAU(m)*CC(Abs(m))-DTAU(-m)*SS(Abs(m)))
    A = ((-1.0)**Abs(m))*(DTAU(m)*Cos(Abs(m)*gGamma)-DTAU(-m)*Sin(Abs(m)*gGamma))
END IF

END FUNCTION A

END

DOUBLE PRECISION FUNCTION B(m)

! USE GLOBAL_VARIABLES
! IMPLICIT NONE
! INCLUDE 'global_vars.txt'

INTEGER m
DOUBLE PRECISION DTAU, CC, SS

If (m .EQ. 0) Then
    B = 0.0
ELSE
    !
    B = ((-1.0)**Abs(m))*(DTAU(m)*SS(Abs(m))+DTAU(-m)*CC(Abs(m)))
    B = ((-1.0)**Abs(m))*(DTAU(m)*Sin(Abs(m)*gGamma)+DTAU(-m)*Cos(Abs(m)*gGamma))
END IF

END FUNCTION B

END

DOUBLE PRECISION FUNCTION S(l, m, mp)
! USE GLOBAL_VARIABLES
! IMPLICIT NONE

INCLUDE 'global_vars.txt'

INTEGER l, m, mp

DOUBLE PRECISION d, A

S = A(m)*((-1.0)**Abs(mp))*d(l, Abs(m), Abs(mp)) +
& d(l, Abs(m), -Abs(mp))

! END FUNCTION S

END

DOUBLE PRECISION FUNCTION T(l, m, mp)

! USE GLOBAL_VARIABLES
! IMPLICIT NONE

INCLUDE 'global_vars.txt'

INTEGER l, m, mp

DOUBLE PRECISION d, B

IF (m .EQ. 0) THEN
    T = 0.0
ELSE
    T = B(m)*((-1.0)**Abs(mp))*d(l, Abs(m), Abs(mp)) -
    & d(l, Abs(m), -Abs(mp))
END IF

! END FUNCTION T

END
DOUBLE PRECISION FUNCTION MAT(l, m, n)

! USE GLOBAL_VARIABLES
!
! IMPLICIT NONE

INCLUDE 'global_vars.txt'

INTEGER l, m, n

DOUBLE PRECISION dResult
INTEGER matIndex
INTEGER i, j, k

matIndex = 0
DO i = 0, m-1
  DO j = 0, i
    DO k = 0, j
      matIndex = matIndex + 1
    END DO
  END DO
END DO

DO i = 0, l-1
  DO j = 0, i
    matIndex = matIndex + 1
  END DO
END DO

matIndex = matIndex + n + 1

MAT = gSKFactors(matIndex)
DOUBLE PRECISION FUNCTION HF(l1, m1, l2, m2)

! USE GLOBAL_VARIABLES

! IMPLICIT NONE

INCLUDE 'global_vars.txt'

INTEGER l1, m1, l2, m2

INTEGER mp

DOUBLE PRECISION sumt

DOUBLE PRECISION dDistance

DOUBLE PRECISION d, S, T, MAT, A

! gGamma = WorksheetFunction.Asin(gM / ((1 - gN**2.0)**0.5))
! gGamma = WorksheetFunction.Acos(-gL / ((1 - gN**2.0)**0.5))

IF (gL .EQ. 0) THEN
  IF (gM .GE. 0) THEN
    gGamma = 3.14159265358979 / 2.0
  ELSE
    gGamma = -3.0*3.14159/2.0
  END IF
ELSE
  gGamma = ATAN2(gM, -gL)
END IF

ELSE
END IF
sumt = 0.0

DO mp = 1, MIN(l1, l2)
   sumt = sumt + (S(l1, m1, mp) * S(l2, m2, mp) + T(l1, m1, mp) * T(l2, m2, mp)) * MAT(Min(l1, l2), Max(l1, l2), Abs(mp))
   
   IF ((l1 .EQ. 0) .AND. (m1 .EQ. 0) .AND. (l2 .EQ. 1) .AND. (m2 .EQ. -1)) THEN
      ! WRITE(*,*) "Sum : ", sumt
   END IF
END IF
END DO
sumt = sumt + 2.0*A(m1)*A(m2)*d(l1, Abs(m1), 0)*d(l2, Abs(m2), 0)*MAT(Min(l1, l2), Max(l1, l2), 0)
sumt = sumt * ((-1.0)**(((l1-l2+Abs(l1 - l2))/2.0)))

HF = sumt

END FUNCTION HF
END

INTEGER FUNCTION MAT2(l, m, n)

! USE GLOBAL_VARIABLES
!
IMPLICIT NONE

INCLUDE 'global_vars.txt'

INTEGER l, m, n

INTEGER matIndex
INTEGER i, j, k
matIndex = 0
DO i = 0, m-1
  DO j = 0, i
    DO k = 0, j
      matIndex = matIndex + 1
    END DO
  END DO
END DO

DO i = 0, l-1
  DO j = 0, i
    matIndex = matIndex + 1
  END DO
END DO

matIndex = matIndex + n + 1

MAT2 = matIndex

! END FUNCTION MAT2
END

SUBROUTINE HF2(l1, m1, l2, m2, iS, iA, iR, iC)
  ! USE GLOBAL_VARIABLES
  ! IMPLICIT NONE
    ! INCLUDE 'global_vars.txt'

  INTEGER l1, m1, l2, m2
  INTEGER iS, iA, iR, iC
INTEGER mp
DOUBLE PRECISION sumt
DOUBLE PRECISION dDistance

DOUBLE PRECISION d, S, T, A
INTEGER iM, MAT2

IF (gL .EQ. 0) THEN
  IF (gM .GE. 0) THEN
    gGamma = 3.14159 / 2.0
  ELSE
    gGamma = 3.0*3.14159/2.0
  END IF
ELSE
  gGamma = ATAN2(gM, -gL)
END IF
ELSE
  gGamma = ATAN2(gM, -gL)
END IF
sumt = 0.0
DO mp = 1, MIN(l1, l2)
  iM = MAT2(Min(l1, l2), Max(l1, l2), Abs(mp))
  gSKCoeffs(iS,iA,iR,iC,iM) = gSKCoeffs(iS,iA,iR,iC,iM) +
  (S(l1, m1, mp)*S(l2, m2, mp) + T(l1, m1, mp)*T(l2, m2, mp))
END DO
iM = MAT2(Min(l1, l2), Max(l1, l2), 0)
  gSKCoeffs(iS,iA,iR,iC,iM) = gSKCoeffs(iS,iA,iR,iC,iM) +
  2.0*A(m1)*A(m2)*d(l1, Abs(m1), 0)*d(l2, Abs(m2), 0)
sumt = ((-1.0)**(((l1-l2+Abs(l1 - l2))/2.0)))
DO mp = 1,20
gSKCoeffs(iS,iA,iR,iC,mp) = sum*t*gSKCoeffs(iS,iA,iR,iC,mp)
END DO

! END SUBROUTINE HF2

END
Appendix B: SPD Fit

Table B.1 shows the best fit spd coefficients for Actinium.

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<th>Best Fit SPD Parameters - Actinium</th>
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<tr>
<td>On-site</td>
<td>a</td>
</tr>
<tr>
<td>s</td>
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<tr>
<td>p</td>
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<tr>
<td>t2g / eg</td>
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<tr>
<td>Hopping</td>
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<tr>
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Table B.1: The best fit Actinium spd coefficients. Since for the cubic structure t2g and eg we set to equal each other, only a single set of coefficients is computed for t2g and eg.
Bibliography


Curriculum Vitae

Joel D. Durgavich was born in New York, but since 2nd grade has lived in Virginia. He graduated from Bishop Ireton High School, Alexandria, Virginia in 1988 and, while attending BI, visited Europe three times with the Bishop Ireton Wind Ensemble. Following his brother’s footsteps, Joel enrolled to the University of Virginia. In addition to pursuing his engineering degree, Joel was a member of “The Award-Winning Virginia Fighting Cavalier Indoor/Outdoor Precision(?) Marching Pep Band, & Chowder Society Review, Unlimited” Pep Band all four years at UVa. He received his Bachelor of Science in Applied Mathematics Engineering from the University of Virginia in 1992. Following graduation, Joel was hired by Systems Planning and Analysis, Inc. in June and was married to his fiancée, Susan, in November. To this day, over twenty years later, he is still gainfully employed by SPA and happily married to Susan. Joel works as a Senior Soft Developer and Analyst at SPA and during his time there has contributed on many projects but two stand out - Stereologer™ and the General Campaign Analysis Model (GCAM™). Stereologer™ was developed under the guidance of Dr. Peter Mouton and is an application which allows computer aided collection and analysis of unbiased data for medical research. GCAM™ was developed under the guidance of Dr. William Lyle and is a modeling and simulation environment which SPA has successfully used to help its clients make important decisions about policy, tactics, and procurement. While employed by SPA, Joel received his Master of Science in Computational Sciences and Informatics from George Mason University in 1998, took a short break and then went back to receive his PhD in Computational Sciences and Informatics from George Mason University in 2012. He looks forward to continuing to contribute to the next generation improvements of Stereologer™, GCAM™, and the NRL-TB programs which were at the core of his dissertation research. Joel and his wife, Susan, have one son, Daniel, who is currently attending his alma mater High School, Bishop Ireton.