Extension of the NRL Tight-Binding Method to Include f orbitals and Applications in Th, Ac, La and Yb

Joel Durgavich,^{*} Shereef Sayed,[†] and Dimitrios Papaconstantopoulos[‡]

*Department of Computational and Data Sciences,
Computational Materials Science Center, George Mason University, Fairfax VA, USA*

(Dated: September 22, 2015)

The original Naval Research Laboratory Tight-Binding(NRL-TB) methodology was designed to only include s, p, and d orbitals in the basis. Because of this limitation, materials which have f orbitals in their valence bands could not be modeled by the current program. In this work we have expanded the NRL-TB method to account for f orbital interactions and used the modified program to investigate Thorium, Actinium, Lanthanum and Ytterbium, materials whose properties are influenced by f electrons. Using the improved program, we were able to develop a set of Slater-Koster polynomial coefficients for these materials that accurately compute properties such as total energy (fcc, bcc, sc, hcp, and diamond), energy bands, density of states, elastic constants, and phonon frequencies.

I. INTRODUCTION

One area of active research is in the rare earth elements (e.g. lanthanides and actinides). The rare earth elements are abundant in some parts of the world but not in others. They are often found in low concentrations, and it is expensive to extract sufficient quantities of them. Understanding their basic properties may be useful in finding ways to replacing them since they have significant applications in magnets, super-conductive devices, batteries, and computers. These materials differ from the lighter elements in the periodic table due to the fact that they contain f electrons. The interaction with the f orbitals has a great impact on the chemical properties of these rare earth elements. To get an accurate picture of the electronic properties of these materials, existing computer codes have been expanded to include the effects of f-orbitals. There have been many investigations of the band structure and total energy of these materials using first-principles methods based on density functional theory(DFT). [1] [2]. In addition to the elaborate DFT applications such as the Linearized Augmented Plane Wave(LAPW) method and the various pseudopotential techniques, the tight-binding(TB) approach is of great interest because it provides a lot of physical insight and efficient ways of handling large-scale calculations. In the case of including f-orbitals in the TB formalism there have been very few implementations due to the complicated Slater-Koster expressions for such orbitals.

In the present work, which is based on a linear combination of atomic orbitals (LCAO) [3] or tight-binding(TB) method, we avoid the task of directly computing the many complex integrals needed in an LCAO approach by adopting the simplification introduced by Slater and Koster(SK) who suggested replacing the LCAO integrals with disposable parameters. [4]

In this method one fits one-electron energy eigenvalues at high-symmetry k-points in the Brillouin zone to first-principles results thus determining the best set of TB parameters for a material. In the original SK paper, only s,p, and d orbitals were considered. In 1974, Lendi expanded the SK process and provided tables that included f-orbitals. [5] Similar expressions were later published by Sharma in 1979, and by Takegahara et. al. [6] [7] Finally in 2004, Podolskiy and Vogl published a compact Hamiltonian formulation to generate the SK parameter expressions. [8] The use of this formulation also allows expansion to higher orbitals if necessary and avoids much of the danger in miscoding the SK matrix. This paper focuses on a tight-binding approach which is essentially the extension of the NRL-TB method to include f-orbitals. [9][10] Previous work has been done in examining the expansion of the NRL Tight-Binding method, by Jones and Albers who modified the NRL Tight-Binding to include f-electron effects and examined the structural parameters, elastic parameters and electronic energy bands for Uranium (U). [11] In a following paper, Jones and Albers included spin-orbit coupling and investigated the density of states (DOS) and band structure for Th, U, and Pu. [12] This latter paper did not succeed in having simultaneously fit the bands and the total energies and having adequate transferability of their parameters to other structures. Our investigation will differ from these previous papers in two significant ways. First, the implementation of the expansion for the NRL Tight-Binding program is done using the compact Hamiltonian matrix formulation developed in [8]. Second, a complete set of material properties is examined once a best fit set of polynomial coefficients is determined. This paper explains the process for the code expansion, offers insights and potential improvements to the fitting process, and presents applications in selected materials i.e. Th, Ac, La and Yb.

^{*} jdurgavi@gmu.edu

[†] ssayed2@gmu.edu

[‡] dpapacon@gmu.edu

II. EXPANSION OF THE NRL TIGHT-BINDING METHOD

The TB method [4] has the advantage of being much faster than first-principles methods because a small matrix is diagonalized (9x9 for spd Hamiltonian and 16x16 when the f-orbitals are included) and there is no self-consistency cycle. The NRL-TB scheme originates from the SK TB method which treats the LCAO integrals as disposable parameters. These parameters are determined by fitting to eigenvalues and total energies of first-principles results. The NRL-TB method extended the SK approach by introducing distance dependent polynomials for the single parameters which make it possible to fit total energies as well as band structures. The advantage of this implementation is that properly chosen TB polynomial coefficients are transferable for the study of other structures that were not fitted. There are three codes associated with the NRL-TB package: the fitting code, the static code, and the molecular dynamics code. For this investigation only the fitting and static code were expanded.

Normally, the total energy of a system is written as

$$E = \sum_i f(\mu - \epsilon_i) \epsilon_i + F[n(r)] \quad (1)$$

where $n(r)$ is the electronic density, ϵ_i is the Kohn-Sham eigenvalue of the i th electronic state, μ is the chemical potential and F contains the remaining parts of the Density Functional Theory (DFT) total energy minus the sum of the one-electron eigenvalues. In other TB approaches F is a sum of pair potentials. However, based on the fact that in DFT one can uniformly shift the energy bands by a constant shift $V_0 = F/N$ (where N is the number of valence electrons) one can apply this shift to the first-principles eigenvalues, which makes the total energy of the system equal to the sum of the shifted eigenvalues.[10] Therefore the shifted eigenvalues are defined as

$$\epsilon'_i = \epsilon_i + V_0 \quad (2)$$

By incorporating this shift, the total energy (1) becomes

$$E = \sum_i f(\mu' - \epsilon'_i) \epsilon'_i \quad (3)$$

The NRL-TB Hamiltonian consists of matrix elements which are calculated from two types of interactions on-site integrals and two-center hopping integrals. The on-site terms affect only the diagonal elements of the Hamiltonian matrix and depend on the density of the atoms. The atom density for the system is defined as

$$\rho_i = \sum_j \exp(-\lambda^2 R_{ij}) F(R_{ij}) \quad (4)$$

where λ is the first fitting coefficient and $F(R_{ij})$ is a cutoff function to limit the number of neighbors used.

This density function is then used to compute the angular momentum dependent on-site terms by

$$h_{il} = a_l + b_l \rho^{2/3} + c_l \rho^{4/3} + d_l \rho^2 \quad (5)$$

where a , b , c , and d are fitting coefficients.

In the original Tight-Binding program, four on-site integrals were considered: s, p, t2g, and eg. This led to the specification of 17 coefficients to define the on-site interactions, one for the λ value and four for each of the s, p, t2g, and eg integrals. With the addition of the f states, an additional four coefficients will be needed for the f on-site interactions raising the total number of on-site coefficients to 21. Note, although t2g and eg have been specified as separate on-site integrals, in practice these terms are set equal to each other to avoid complications in fitting and transferability with non-cubic crystal structures.

The two-center integral introduces two contributions: hopping integrals 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 i.e.

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

In the monatomic case, symmetry considerations remove four of the integrals i.e.

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

So, for the monatomic case, we have ten independent two-center integrals which gave rise to twenty fitting parameters, ten for the hopping integrals and ten for the overlap integrals. Now the addition of the f-orbitals introduces 16 more integrals as follows:

$$sf\sigma, pf\sigma, pf\pi, df\sigma, df\pi, df\delta, fs\sigma, fp\sigma, \\ fp\pi, fd\sigma, fd\pi, fd\delta, ff\sigma, ff\pi, ff\delta, ff\gamma$$

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 a total of twenty SK parameters are needed for the hopping integrals and an additional twenty SK parameters are needed to define the overlap integrals. To allow the fitting results to be transferable to other structures, the parameters are not defined by a single value but instead are defined by a quadratic polynomial times an exponential function as follows:

$$H_{l'l''\mu} = \\ (e_{l'l''\mu} + f_{l'l''\mu} R + g_{l'l''\mu} R^2) \exp(-h_{l'l''\mu}^2 R) F(R) \quad (6)$$

R represents the distance between two atoms and $F(R)$ is the same cut-off function as described earlier. A similar expression describes the overlap integrals. 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 160, four coefficients for each of the 20 hopping and 20 overlap SK parameters. In summary, 181 coefficients are needed to build the complete non-orthogonal on-site and two-center integrals in the monatomic case, 21 for the on-site contributions and 160 for the two-center contributions.

Our computer code is designed to use the parameters for a non-orthogonal Hamiltonian. However, in the present work we did not include the overlap matrix which reduced the number of disposable two-center parameters fit to 80. Between the exclusion of the overlap integrals and the simplification in the on-site integral parameters by setting t_{2g} equal eg, a total of 97 fitting coefficients were used. Although in a few of our previous papers using spd Hamiltonians we used non-orthogonal basis, in this paper we opted to use orthogonal Hamiltonians for simplicity and due to the fact that we found almost no improvement in our fits by employing non-orthogonality.

The NRL-TB program uses a Levenberg-Marquardt least squares algorithm to minimize the total energy and eigenvalue differences between the TB and first-principles calculations. The possibility of using other minimization procedures such as Monte Carlo or genetic algorithms goes beyond the scope of this paper. Not finding a possible absolute minimum does not prevent having a good fit for the transferability applications presented in this work. The potential mixing of orbital character and symmetry is avoided by block-diagonalizing the Hamiltonian as discussed in Sec. III.

The most important change to the NRL fitting and static code was to introduce an analytic way to compute the Hamiltonian matrix elements as described by [8]. Within this 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 given below.

$$\begin{aligned}\bar{Y}_{l,0}(\theta, \phi) &= Y_{l,0}(\theta, \phi) \\ m > 0 : \bar{Y}_{l,m}(\theta, \phi) &= \sqrt{2}(-1)^m \text{Re}Y_{l,m}(\theta, \phi) \\ m < 0 : \bar{Y}_{l,m}(\theta, \phi) &= \sqrt{2}(-1)^m \text{Im}Y_{l,m}(\theta, \phi)\end{aligned}\quad (7)$$

With the above definition, the basis orbital functions become

$$\langle r | l, m, R \rangle = \bar{Y}_{l,m}(\theta, \phi) \rho(|r - R|) \quad (8)$$

and the Hamiltonian matrix elements become

$$\begin{aligned}\langle l_1, m_1, 0 | H | l_2, m_2, R_\xi \rangle &= \\ \int dr \bar{Y}_{l_1, m_1}(\theta, \phi) \rho_1(|r|) H \bar{Y}_{l_2, m_2}(\theta, \phi) \rho_2(|r - R_\xi|)\end{aligned}\quad (9)$$

Upon integration, the analytic equations for the Hamiltonian matrix elements are

$$\begin{aligned}\langle l_1, m_1, 0 | H | l_2, m_2, R_\xi \rangle &= (-1)^{(l_1 - l_2 + |l_1 - l_2|)/2} \\ &\left\{ \sum_{m'}^{l <} \left[S_{m_1, |m'|}^{l_1} S_{m_2, |m'|}^{l_2} + T_{m_1, |m'|}^{l_1} T_{m_2, |m'|}^{l_2} (l < l' > |m'|) \right] \right\} \\ &+ 2A_{m_1} A_{m_2} d_{|m_1|, 0}^{l_1} d_{|m_2|, 0}^{l_2} (l < l' > 0) \\ S_{m, |m'|}^l &= A_m \left[(-1)^{|m'|} d_{|m|, |m'|}^l + d_{|m|, -|m'|}^l \right] \\ T_{m, |m'|}^l &= (1 - \delta_{m0}) B_m \left[(-1)^{|m'|} d_{|m|, |m'|}^l - d_{|m|, -|m'|}^l \right] \\ A_m &= (-1)^{|m|} [\tau(m) \cos(|m|\gamma) - \tau(-m) \sin(|m|\gamma)] \\ B_m &= (-1)^{|m|} [\tau(m) \sin(|m|\gamma) - \tau(-m) \cos(|m|\gamma)] \\ \tau(m) &= 1 \text{ if } m \geq 0 \text{ or } 0 \text{ if } m < 0 \\ d_{m, m'}^l &= \left(\frac{1+N}{2} \right)^l \left(\frac{1-N}{1+N} \right)^{\frac{m-m'}{2}} \\ &[(l+m')! (l-m')! (l+m)! (l-m)!]^{1/2} \\ &\sum_{t=0}^{2l+1} \left[\frac{(-1)^t}{(l+m'-t)! (l+m-t)! (l+m-m')!} \left(\frac{1-N}{1+N} \right)^t \right]\end{aligned}\quad (10)$$

Note that the summation is for all non-negative factorials

The symbol d above represents the rotation matrices and the N is the direction cosine with respect to the z -axis. The $\langle l_1, m_1, 0 | H | l_2, m_2, R_\xi \rangle$ represents the two-center Hamiltonian matrix elements. The $(l <, l' >, |m'|)$ factors in the Hamiltonian matrix elements are place holders for low level integrals which will be replaced by disposable parameters during the fitting process.

Computing the Hamiltonian matrix elements in this fashion reduces the speed of the program, but minimizes the likelihood of errors in the coding. In addition, this general method will have the advantage of allowing the program to be extended to include g -orbitals.

III. DISCUSSION OF THE FITTING PROCESS

The modified Tight-Binding program was used to determine the polynomial coefficients that appear in equations 4-6 of Section II. During the fitting process three sets of data are included. All of these data are obtained from first-principles LAPW calculations. The first set of data to fit is the energy bands for a uniform mesh of k -points in the Brillouin zone and different volumes and crystal structures. A good energy bands fit should have an RMS error on the order of 10 mRy for all bands considered. The second set of data to be fit is the total energy as a function of volume and structure. The desired total energy RMS error is on the order of 1 mRy. In the construction of the input files, all of the energy values are shifted relative to the lowest structure energy which in the case of Th, and Ac is the fcc. The last fitting data set is the eigenenergies from a block diagonalized Hamiltonian at high symmetry points Γ , X, and L for the fcc structure as shown in Table I. As has been pointed out in the review article by Papaconstantopoulos and his book and also emphasized by Jones and Albers, it is important

to include block-diagonalization to avoid the incorrect assignment of eigenvalues to angular momentum character and symmetry.[9][11][13]

At high symmetry points, the full Hamiltonian matrix is broken down into smaller blocks as shown in Table I to insure 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 at some of the symmetry points to account for the mixing of f-orbital character with s, p, and d orbitals. For example in the fcc Γ point, the Hamiltonian is broken into four smaller matrices, a 1x1 matrix with the s character eigenvalue, a 3x3 matrix with the three t_{2g} character eigenvalues, a 2x2 matrix with the two e_g character eigenvalues, and a 10x10 matrix which contains the 10 eigenvalues with mixed p and f character. The first-principles results needed for our TB parametrizations, we generated using the LAPW program that was written at NRL by Singh and Krakauer with minor modifications by Mehl over the years. The exchange and correlation functional used was the Generalized Gradient Approximation(GGA) for Th, and the Hedin-Lundqvist form of the Local Density Approximation(LDA) for Ac. The reason for this difference was to choose those that gave the best agreement with experiment for the respective fcc lattice constants. During the fitting process we fit not only the fcc LAPW data for the most stable structure, but also include other structures(e.g. bcc, sc, dia). This information is needed so that the structure energy ordering would be correct. For Th we fitted 18 fcc volumes, 5 bcc volumes, 5 sc volumes, and 5 diamond volumes. For Ac, 6 fcc volumes, 6 bcc volumes, 7 sc volumes, and 5 diamond volumes were fit. After determining the fitting coefficients, various quantities of the material are calculated and non-fitted structures are predicted using the 'static' component of the package.

Although both orthogonal and non-orthogonal fits can be performed using the NRL-TB program, only an orthogonal fit was done for this work. As mentioned above this choice was made for reducing the number of adjustable fitting coefficients with no significant loss of accuracy in the fits. For the Thorium fit, the total energy error was 2 mRy and the average band error across 11 bands at the equilibrium lattice location was 17 mRy. For the Actinium fit, the total energy error was 0.3 mRy and the average band error across 11 bands was 18 mRy. Shown in Tables II and III are the fit coefficients of Thorium and Actinium respectively.

IV. GROUND-STATE BEHAVIOR AND PHASE STABILITY

Given the above fitting coefficients, the NRL static program was used to examine the different crystal structures as shown in Figure 1 and Figure 2. From Figures 1 and

FIG. 1: Total Energy as a function of Volume per Atom - Th

FIG. 2: Total Energy as a function of Volume per Atom - Ac

2 showing the structural energies of Th and Ac, one can see that the lowest energy corresponds to the fcc lattice and immediately higher we find the hcp energies and after that the bcc energies which were well fitted to the LAPW energies and in agreement with the experimental fact that both Th and Ac have fcc ground state. Total energies for hcp, L12, and A15 structures were calculated in addition to the structures fit. For both Th and Ac, the hcp energy graph produced the reasonable result that the minimum hcp structure energy would fall between the bcc and fcc structures. The energies for the other structures shown in the figures are much higher as expected concluding that our TB description for these elements is robust.

Applying a quadratic fit to the static data, we determine for the minimum energy the equilibrium lattice constant for each type of structure. A summary of those values and how they compare to the LAPW results is shown in Table IV. The corresponding experimental lattice parameters for the fcc structure are 9.60 Bohr for Th and 10.04 Bohr for Ac. For Th the lattice constant from both LAPW and TB are in perfect agreement with the measurement. However for Ac, both our LAPW and TB results overestimate the lattice parameter by about 3%. As we mentioned earlier for Ac we present LDA results while the GGA result gives an even larger value for the

State	k-point	Matrix
Γ_1 Γ_{12} Γ_2' Γ_{25}' $\Gamma_{15} + \Gamma_{25}$	0,0,0	$\begin{bmatrix} [H_{1,1}] \\ [H_{8,8}] \\ [H_{14,14}] \\ [H_{5,5}] \\ \begin{bmatrix} H_{2,2} & H_{2,11} & H_{2,15} \\ H_{11,2}^* & H_{11,11} & H_{11,15} \\ H_{15,2}^* & H_{15,11}^* & H_{15,15} \end{bmatrix} \end{bmatrix}$
X_1 X_2 X_2' X_3 X_3' X_4' X_5 X_1'	$\frac{2\pi}{a} (100)$	$\begin{bmatrix} \begin{bmatrix} H_{1,1} & H_{1,9} \\ H_{1,1}^* & H_{9,9} \end{bmatrix} \\ [H_{8,8}] \\ [H_{14,14}] \\ [H_{7,7}] \\ [H_{13,13}] \\ \begin{bmatrix} H_{4,4} & H_{4,10} \\ H_{10,4}^* & H_{10,10} \end{bmatrix} \\ [H_{5,5}] \\ \begin{bmatrix} H_{2,2} & H_{2,11} & H_{2,15} \\ H_{11,2}^* & H_{11,11} & H_{11,15} \\ H_{15,2}^* & H_{15,11}^* & H_{15,15} \end{bmatrix} \end{bmatrix}$
L_1 L_3 $L_3' + L_2'$ $L_3' + L_1'$	$\frac{2\pi}{a} \left(\frac{1}{2} \frac{1}{2} \frac{1}{2} \right)$	$\begin{bmatrix} H_{1,1} & \frac{1}{\sqrt{3}} [H_{1,5} + H_{1,6} + H_{1,7}] \\ \frac{1}{\sqrt{3}} [H_{1,5}^* + H_{1,6}^* + H_{1,7}^*] & \frac{1}{3} \begin{bmatrix} H_{5,5} + H_{6,6} + H_{7,7} + 2 * (H_{5,6} + H_{5,7} + H_{6,7}) \end{bmatrix} \end{bmatrix}$ $\begin{bmatrix} \frac{1}{2} [H_{5,5} - 2H_{5,6} + H_{6,6}] & \frac{1}{\sqrt{2}} [H_{5,8} - H_{6,8}] \\ \frac{1}{\sqrt{2}} [H_{5,8}^* - H_{6,8}^*] & H_{8,8} \end{bmatrix}$ <div>upper diagonal elements listed</div> $\begin{aligned} M_{11} &= \frac{1}{2} [H_{2,2} + H_{3,2} + H_{2,3} + H_{3,3}] \\ M_{12} &= \frac{\sqrt{(2)}}{2} [H_{2,4} + H_{3,4}] \\ M_{13} &= \frac{\sqrt{(2)}}{2} [H_{2,10} + H_{3,10}] \\ M_{14} &= \frac{1}{2} [H_{2,11} + H_{3,11} + H_{2,12} + H_{3,12}] \\ M_{15} &= \frac{\sqrt{(2)}}{2} [H_{2,14} + H_{3,14}] \\ M_{16} &= \frac{1}{2} [H_{2,15} + H_{3,15} - H_{2,16} - H_{3,16}] \\ M_{22} &= H_{4,4} \\ M_{23} &= H_{4,10} \\ M_{24} &= \frac{\sqrt{(2)}}{2} [H_{4,11} + H_{1,12}] \\ M_{25} &= H_{4,14} \\ M_{26} &= \frac{\sqrt{(2)}}{2} [H_{4,15} - H_{4,16}] \\ M_{33} &= H_{10,10} \\ M_{34} &= \frac{\sqrt{(2)}}{2} [H_{10,11} + H_{10,12}] \\ M_{35} &= H_{10,14} \\ M_{36} &= \frac{\sqrt{(2)}}{2} [H_{10,15} - H_{10,16}] \\ M_{44} &= \frac{1}{2} [H_{11,11} + H_{12,11} + H_{11,12} + H_{12,12}] \\ M_{45} &= \frac{\sqrt{(2)}}{2} [H_{11,14} - H_{12,14}] \\ M_{46} &= \frac{1}{2} [H_{11,15} + H_{12,15} - H_{12,15} - H_{12,16}] \\ M_{55} &= H_{14,14} \\ M_{56} &= \frac{\sqrt{(2)}}{2} [H_{14,15} - H_{14,16}] \\ M_{66} &= \frac{1}{2} [H_{15,15} - H_{16,15} - H_{16,16} + H_{16,16}] \end{aligned}$ <div>upper diagonal elements listed</div> $\begin{aligned} M_{11} &= \frac{1}{2} [H_{2,2} - H_{3,2} - H_{2,3} + H_{3,3}] \\ M_{12} &= \frac{1}{2} [H_{2,11} - H_{3,11} - H_{2,12} + H_{3,12}] \\ M_{13} &= \frac{\sqrt{2}}{2} [H_{2,13} - H_{3,13}] \\ M_{14} &= \frac{1}{2} [H_{2,15} - H_{3,15} + H_{2,16} - H_{3,16}] \\ M_{22} &= \frac{1}{2} [H_{11,11} - H_{12,11} - H_{11,12} + H_{12,12}] \\ M_{23} &= \frac{\sqrt{2}}{2} [H_{11,13} - H_{12,13}] \\ M_{24} &= \frac{1}{2} [H_{11,15} - H_{12,15} + H_{11,16} - H_{12,16}] \\ M_{33} &= H_{13,13} \\ M_{34} &= \frac{\sqrt{2}}{2} [H_{13,15} + H_{13,16}] \\ M_{44} &= \frac{1}{2} [H_{15,15} + H_{16,15} + H_{15,16} + H_{16,16}] \end{aligned}$

TABLE I: Block Diagonalization of the 16 x 16 Hamiltonian for high-symmetry fcc k-points Γ , X, and L

Best Fit Parameters - Thorium				
λ	1.02539			
On-site	a	b	c	d
s	0.13797	6.27480	178.09594	-1249.79025
p	0.03488	22.02659	-70.46032	-409.25331
t2g / eg	0.14610	3.02598	28.84294	0.09348
f	0.08457	6.28333	-52.83231	374.57747
Hopping	e	f	g	h
ss σ	51.57930	-8.39361	-0.44661	0.94140
sp σ	32.36753	-3.96015	-0.57008	0.92637
pp σ	-1.52404	-6.67075	1.46760	0.89794
pp π	11.30628	9.19351	-2.00433	0.91880
sd σ	141.65242	-18.94744	-2.93647	1.06296
pd σ	-69.21398	2.67500	2.30603	0.97590
pd π	24.52695	-1.16931	-1.18063	1.00234
dd σ	102.95988	-19.45823	-3.18257	1.04303
dd π	2.96755	-1.11881	0.27813	0.86898
dd δ	10.58619	-4.68342	0.35179	0.91895
sf σ	-6.94685	1.75797	0.73778	1.00008
pf σ	-13.27169	-7.29476	1.49611	0.99452
pf π	-35.98929	0.10714	1.15616	1.02858
df σ	-7.25622	-1.14161	0.16676	0.90957
df π	2.88063	-0.22867	-0.32686	0.96495
df δ	44.26243	1.66673	-1.21896	1.00594
ff σ	-128.52489	9.84990	2.98954	1.09855
ff π	-9.30697	-0.61043	-0.10979	1.00005
ff δ	4.62519	-0.29235	-0.00571	0.91293
ff ϕ	-14.73599	2.49432	-0.05322	1.00003

TABLE II: Thorium Parameters

Best Fit Parameters - Actinium				
λ	0.96988			
On-site	a	b	c	d
s	-0.05555	5.87648	39.49576	210.93252
p	0.19592	2.90985	18.73883	891.20419
t2g / eg	0.17455	2.32269	11.36571	-78.38154
f	0.49724	2.13899	-78.30429	816.19415
Hopping	e	f	g	h
ss σ	36.33311	-20.71338	-1.10101	1.05840
sp σ	26.26251	-3.09216	-0.13358	0.81718
pp σ	-24.88447	-25.96894	3.80238	0.88537
pp π	1.18555	0.66205	-0.16589	0.83730
sd σ	95.19860	-11.49345	-1.97917	1.00666
pd σ	-55.32887	-1.14782	1.57759	0.91694
pd π	174.33604	-15.09062	-4.53885	1.07579
dd σ	107.68183	-7.98824	-3.17266	1.00040
dd π	13.88193	-4.37929	0.52494	0.88580
dd δ	-2.03544	1.45303	-0.19582	0.89723
sf σ	-15.46321	-0.98403	0.48900	0.94881
pf σ	19.82031	1.25033	0.14207	0.99930
pf π	-36.34654	-0.53422	1.05330	0.92542
df σ	-46.29772	-3.91273	1.87624	0.91514
df π	0.02777	-0.30087	-0.08168	0.83093
df δ	-13.78257	0.44064	0.37449	0.96750
ff σ	7.93720	-2.49652	0.28746	0.81554
ff π	-182.08514	64.33363	-5.35936	0.92758
ff δ	218.29982	-15.18728	3.11179	1.14192
ff ϕ	-182.50301	-1.36521	0.09305	1.13197

TABLE III: Actinium Parameters

	Th LAPW	Th TB	Ac LAPW	Ac TB
SC	0.066 Ry 6.20 Bohr	0.062 Ry 6.40 Bohr	0.0492 Ry 6.81 Bohr	0.051 Ry 6.79 Bohr
BCC	0.011 Ry 7.60 Bohr	0.015 Ry 7.52 Bohr	0.0096 Ry 8.28 Bohr	0.010 Ry 8.30 Bohr
FCC	0.000 Ry 9.60 Bohr	0.000 Ry 9.61 Bohr	0.0000 Ry 10.40 Bohr	0.000 Ry 10.44 Bohr
HCP	-	0.007 Ry c = 10.93 Bohr c/a = 1.7	-	0.002 Ry c = 11.77 Bohr c/a = 1.7
DIA	-	0.149 Ry 13.95 Bohr	-	0.125 Ry 14.79 Bohr

TABLE IV: Energy and lattice constant comparison

FIG. 3: Bain Path for Th and Ac

lattice constant.

Another investigation into the stability of the fit would be to examine structures of lower symmetry. Figure 3 below shows the energy of Thorium and Actinium under a volume conserving tetragonal strain, called the Bain path. This figure shows the energy, at the calculated fcc equilibrium volume, as a function of c/a . The energy is properly at a minimum for the fcc lattice ($c/a = \sqrt{2}$) and at a maximum for the bcc lattice ($c/a = 1$) in both elements.

V. ELECTRONIC STRUCTURE

Both the energy bands and the density of states (DOS) match well the LAPW data for the fcc structure at equilibrium for both materials. This further verifies the very good quality of the fits. In Figure 4 and Figure 5, we note that the occupied TB bands match the LAPW bands well along all directions with the exception of Th showing a small discrepancy along the Λ and Σ directions. We also see in the Figs 6 and 7 a comparison of TB and LAPW total DOS fit showing a very good match of the peaks including the sharp peaks above the Fermi level indicating the f-states. It is interesting to note that in Ac the f-DOS are located about 0.5 Ry above the Fermi level while in Th the f-states come down to about 0.2 Ry above the Fermi level. This is an expected trend of the position of the Fermi level entering the f-bands as one moves to

heavier actinides. To further check the quality of the fit in terms of the eigenvectors it produces, the d-like and f-like DOS for Th are shown in Figures 8 and 9. Considering the differences in the basis sets the agreement between TB and LAPW is very good.

FIG. 4: Band Plot LAPW-TB for Thorium

FIG. 5: Band Plot LAPW-TB for Actinium

FIG. 6: DOS Plot LAPW-TB for Thorium

VI. ELASTIC CONSTANTS

$C_{11} - C_{12}$ is computed by performing a least squares fit to the energy data generated by applying an orthorhombic strain to the equilibrium fcc lattice and the equation

FIG. 7: DOS Plot LAPW-TB for Actinium

FIG. 8: d-like DOS Plot LAPW-TB for Thorium

FIG. 9: f-like DOS Plot LAPW-TB for Thorium

below [14] gives the strained total energy linear dependence on the squared of the strain e :

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

Similarly the C_{44} elastic constant can be determined by applying a volume conserving monoclinic strain to the equilibrium fcc lattice using the following expression:

$$E = E_0 + \frac{1}{2}VC_{44}e^2 + O[e^4] \quad (12)$$

The bulk modulus is calculated from the second derivative of the energy with respect to volume i.e.

$$B = -V \frac{d^2E}{dV^2} \quad (13)$$

FIG. 10: Energy v. Square of Displacement used to determine the elastic constants $C_{11} - C_{12}$ and C_{44} for Th and Ac, as indicated.

and is also related to the elastic constants by the formula:
 $B = (C_{11} + 2C_{12})/3$

Figure 10 show the linear dependence of the distorted energy versus the displacement e^2 from which we calculated the elastic constants $C_{11} - C_{12}$ and C_{44} . The summary of the elastic constant information in Table V shows good agreement with experimental data for Th. We did not find experimental results to compare our Ac results. In addition to fitting experimental data well, the results confirm that the fcc structure is mechanically stable since both $C_{11} - C_{12}$ and C_{44} have positive values.

VII. PHONON FREQUENCIES

The experimental phonon frequencies for Thorium were obtained from Reese et al. [15]. These results are compared with our calculations on Table VI. The agreement is satisfactory especially since no phonon frequencies were included in our fitting database. Our results for Ac

Thorium		
	Experimental	TB Ortho
Bulk	54.00 GPa	47.30 GPa
$C_{11} - C_{12}$	62.89 GPa	66.30 GPa
C_{44}	31.00 GPa	33.82 GPa
Actinium		
	Experimental	TB Ortho
Bulk	-	25.88 GPa
$C_{11} - C_{12}$	-	23.00 GPa
C_{44}	-	22.68 GPa

TABLE V: Elastic Constants of Th and Ac

are also given in Table 20 but no experimental values are available to compare.

	Direction	Th - Exp	Th - TB	Ac - TB
D1	Longitudinal	2.417 THz	2.95 THz	1.56 THz
D5	Transverse	1.585 THz	1.97 THz	1.04 THz
L2	Longitudinal	3.240 THz	2.78 THz	1.35 THz
L3	Transverse	1.280 THz	1.94 THz	0.53 THz
S1	Longitudinal	3.056 THz	3.39 THz	1.71 THz
S2	Transverse	2.241 THz	1.94 THz	1.12 THz
S3	Transverse	1.500 THz	2.65 THz	1.35 THz
W2	Π'	2.875 THz	2.34 THz	1.83 THz
W5	Λ	2.215 THz	3.35 THz	1.58 THz
X3	Longitudinal	3.474 THz	2.03 THz	2.35 THz
X5	Transverse	2.259 THz	3.34 THz	1.84 THz

TABLE VI: Phonon frequencies comparison

VIII. VACANCY FORMATION

The critical feature of the vacancy formation is that its value to be positive to indicate the stability of the complete crystal structure than with a vacancy. The vacancy formation energy for the fcc structure was tested for convergence with respect to the size of the supercell and the number of k-points used for Th. The results of this test are shown in Table VII from which we conclude that doing these calculations at the Gamma point would require a lot more than 343 atoms in the unit cell to converge. It appears that a calculation with 216-atom cell and 20 k-points gives satisfactory convergence. The calculations were done using the following equation:

$$E_{vacancy} = E_{N-1} - (N-1)/N E_N \quad (14)$$

where E_N is the energy of the N-atom supercell and E_{N-1} the energy with one atom removed.

In Table VII, the (N-1) atom energy is unrelaxed so the vacancy formation energy shown is expected to be lower upon relaxation. This would be consistent with the experimental value of 0.0695 Ry given by Ghorai and Sen [16] for Th. For Ac we did not find a measured value of vacancy formation energy. Our calculated value for a 125-atom supercell is 0.1239 Ry which is very close to that of Th as expected.

No of atoms	Gamma	6 k-pts	20 k-pts	89 k-pts
64	0.13418	0.13878	0.14608	0.14684
125	0.11030	0.13167	0.13812	0.13783
216	0.10425	0.13868	0.14119	0.14090
343	0.12638	0.13733	0.13993	0.13980

TABLE VII: Vacancy formation energy in Ry. Convergence test.

IX. LANTHANIDES (YB AND LA)

In the lanthanides, as discussed in [13], the position of the f-bands with respect to the Fermi level critically affects obtaining the correct equilibrium volume with standard density functional theory (DFT). It turns out that in

La where the f-bands are clearly located above E_F DFT works well. However, as we proceed from Ce to Tm, E_F is within the very narrow f-bands and as a result DFT cannot find the appropriate minimum of the total energy. We have found that a reasonable equilibrium volume can be calculated for these materials by pushing the f-electrons into the core and use only the s- and d-electrons in the valence [17] [18]. For Yb and La the f-bands are clearly below E_F and the calculated equilibrium volume is reasonable. In this work we performed a TB fit to LAPW results for La and Yb. The NRL-TB coefficients are given in Tables VIII and IX.

In the case of Yb, we found that the APW calculations (with LDA) give an equilibrium constant of $9.2a.u.$, which is too small in comparison to the experimental value of $10.36a.u.$ This is due to the proximity of E_F to the f-bands as is shown in Figure 12a. Therefore, in the case of Yb, in order to construct a useful tight-binding parameterization, we applied the empirical procedure of shifting the total energies of fcc and bcc so that the fcc minimum corresponded to an APW lattice parameter of $10.2a.u.$ The TB fit was excellent, with an RMS error of $0.2mRy$ for the total energy, and $20mRy$ for the energy bands. This gives a bulk modulus of $26.4GPa$, which is in reasonable agreement to the measured value of $13.3GPa$. The resulting total energy versus volume graph is given in Figure 11, showing correctly the fcc lattice as the ground state, followed closely by the bcc, with the simple cubic at very high energy. The NRL-TB energy bands and DOS of Yb are shown in Figures 12 and 13 where one notes the narrow pronounced f-like peak of the DOS just below the Fermi level, which goes as high as $1400states/Ry$. The value of the DOS at E_F is $1.262states/Ry$, which is 81% s-like and could translate to an electronic specific heat coefficient of $\gamma = 0.219 mJ mol^{-1} deg^{-2}$. The calculated elastic constants of Yb are $C_{11} - C_{12} = 14.95GPa$ and $C_{44} = 36.17GPa$; however, we could not find experimental results of Yb to compare against this result.

For La, we fitted the LAPW results of Nixon et. al. [17]. The NRL-TB parameters are listed in Table IX. Using these parameters, we reproduce very well the LAPW total energies with an RMS error of $0.3mRy$. The results are shown in Figure 14. We note the same ordering of the crystal structures with dhcp as the ground state, the fcc below hcp, and bcc above. The resulting lattice parameters $a = 6.84a.u.$ and $c = 22.07a.u.$ are in good agreement with the experimental values $a = 7.13a.u.$ and $c = 22.83a.u.$, respectively.

X. SPIN-ORBIT

Following [8], we also investigated the effect of spin-orbit splitting. For the d spin-orbit parameter we used the value $0.01123 Ry$ found in the atomic structure tables of Herman and Skillman [19]. For the f orbitals we estimated the spin-orbit parameter by examining the splitting of states found at high symmetry points in an LAPW

Best Fit Parameters - Ytterbium				
λ	1.04122			
On-Site	a	b	c	d
s	-0.04930	0.79689	6.46665	-210.63905
p	-0.04424	21.34416	-215.70670	1428.70305
t2g / eg	0.20409	9.17287	-163.51514	2088.35168
f	0.01726	-0.08042	1.75891	36.33139
Hopping	e	f	g	h
ss σ	-156.05449	58.47202	-5.65288	1.00000
sp σ	32.44057	-37.19317	5.27605	1.00000
pp σ	-163.24708	42.28728	-0.28600	1.00000
pp π	-726.73547	223.50630	-17.76907	1.00000
sd σ	11.01946	0.27071	-0.24918	1.00000
pd σ	-114.68819	-10.01741	3.69160	1.00000
pd π	41.96142	-8.01471	-1.12375	1.00000
dd σ	1423.55035	-385.16821	23.92834	1.00000
dd π	-870.20673	256.02916	-18.61348	1.00000
dd δ	51.78076	-25.82523	3.21953	1.00000
sf σ	-14.02107	2.41409	-0.02997	1.00000
pf σ	-2.19099	-0.61542	0.10054	1.00000
pf π	6.49367	-2.35432	0.46633	1.00000
df σ	-99.54669	0.87188	2.18543	1.00000
df π	-8.76881	1.96826	0.14863	1.00000
df δ	-14.70211	-2.40990	0.80658	1.00000
ff σ	-141.62626	40.69058	-2.91103	1.00000
ff π	18.01253	-5.28774	0.37780	1.00000
ff δ	-150.01693	41.42821	-2.83597	1.00000
ff ϕ	30.25456	-8.61783	0.66593	1.00000
fs σ	0.00100	0.00000	0.00000	1.00000

TABLE VIII: Ytterbium Parameters

Best Fit Parameters - Lanthanum				
λ	0.95874			
On-Site	a	b	c	d
s	-0.05391	13.66172	-274.23995	1680.66509
p	-1.37808	262.09792	-3691.93146	46956.29098
t2g / eg	-0.47945	28.92555	-331.74698	1171.67655
f	-0.87950	45.20731	-618.94003	2786.48966
Hopping	e	f	g	h
ss σ	-476.10571	146.06502	-11.05602	0.91000
sp σ	753.42516	-198.27634	9.59277	0.95849
pp σ	-2763.20030	31.01927	187.21204	1.06995
pp π	351.90936	-46.59968	-16.93881	1.06480
sd σ	-1475.64171	457.88060	-34.26570	1.11232
pd σ	948.10600	-265.47502	14.48569	0.96274
pd π	483.84058	-123.93907	10.68820	0.97226
dd σ	-114.05509	-4.29371	4.34058	1.03248
dd π	299.17428	-6.60314	-6.59515	1.11748
dd δ	62.18431	-2.99131	-2.13177	1.01693
sf σ	-301.80192	22.81707	3.58022	1.04800
pf σ	13.41659	-43.09537	5.93636	0.88519
pf π	-336.55389	126.02228	-15.75224	1.01983
df σ	-54.56592	3.30600	1.06932	1.00957
df π	12.23268	155.60007	-30.12897	1.17637
df δ	16.86849	1.12542	-0.46940	1.01505
ff σ	-104.05321	7.65088	1.11067	1.02697
ff π	-45.18775	0.95172	0.93051	1.00445
ff δ	2.26949	0.53768	0.12266	1.03973
ff ϕ	24.03992	-1.87605	-0.49034	1.03161
fs σ	1.78851	0.53986	0.12104	

TABLE IX: Lanthanum Parameters

calculation that included the spin-orbit effect. The value

FIG. 11: Total Energy Fit of Ytterbium

(a) APW bands of Yb at lattice constant $a=10.2$ a.u.

(b) NRL-TB bands for Yb

FIG. 12: Comparison of APW and NRL-TB band structure for Yb

chosen was 0.01 Ry which turns out to be close to that of the d-orbitals. Figure 15 shows a bands-plot with and without spin-orbit splitting. At first glance this figure does not reveal important differences.

However, one thing not seen on this graph is that the lower d and f triplets at the Γ point become mixed due to the very small gap between those eigenvalues. This is a deviation from the LAPW results which

FIG. 13: NRL-TB Total Density of States of Yb

FIG. 14: Total energy per atom for La

FIG. 15: FCC bands with spin-orbit

maintain the separation of the lower d and f eigenvalues. The mapping of eigenvalues from non-spin orbit to spin-orbit results at high-symmetry points is shown in Table X.

XI. SUMMARY

The NRL-TB method was successfully expanded to include the effects of f-orbital electrons and with this expanded application it was possible to fit the LAPW results for Thorium, Actinium, Ytterbium, and Lan-

X		L	
-0.2146 (1)	-0.2149 (2)	-0.2186 (1)	-0.2189 (2)
-0.1866 (1)	-0.1868 (2)	0.0518 (1)	0.0501 (2)
0.1576 (1)	0.1442 (2)	0.0967 (2)	0.0861 (2)
0.1557 (2)	0.1529 (2)	0.1070 (2)	0.1070 (2)
0.1806 (1)	0.1544 (2)	0.1499 (1)	0.1300 (2)
0.2337 (2)	0.1855 (2)	0.1372 (2)	0.1320 (2)
0.2498 (1)	0.2346 (2)	0.1575 (2)	0.1575 (2)
0.4820 (1)	0.2412 (2)	0.2563 (2)	0.2560 (2)
0.5274 (1)	0.2538 (2)	0.2921 (1)	0.2947 (2)
0.7527 (2)	0.4821 (2)	0.3256 (1)	0.3271 (2)
	0.5270 (2)	0.6495 (2)	0.6447 (2)
	0.7473 (2)		0.6546 (2)
	0.7589 (2)		
Gamma			
-0.3506 (1)	-0.3506 (2)		
0.0411 (1)	0.0396 (2)		
0.1076 (3)	0.1011 (4)		
	0.1188 (2)		
0.1314 (3)	0.1210 (4)		
	0.1481 (2)		
0.2917 (3)	0.2876 (2)		
	0.2964 (4)		
0.4172 (2)	0.4181 (4)		

TABLE X: Spin-Orbit Splitting Correspondence. The numbers in parenthesis indicate degeneracies

thanum materials whose properties are dependent on the f-orbitals. The Hamiltonian derived in this fit is orthogonal and reproduces very well equilibrium quantities, energy bands and DOS for all fitted structures. In addition it reproduces well, in agreement with experiment, non-fitted quantities such as elastic constants, phonon frequencies, vacancy formation energies and the effects of spin-orbit interaction. In future work molecular dynamics application will be considered and other f-orbital-dependent materials within the lanthanides and actinides will be investigated. A website describing the present extension of our tight-binding method is under construction.

Acknowledgments We thank Dr. Michael Mehl for many useful discussions. This work was partially supported by ONR Grant No N00014-09-1-1025.

-
- [1] B. Johansson and A. Rosengren. *Phys. Rev.*, B11,2836, (1975).
- [2] R. C. Albers M. D. Jones, J. C. Boettger and D. J. Singh. *Phys. Rev. B*, 61,4644, (2000).
- [3] F. Bloch. *Z. Physik*, 52,555, (1928).
- [4] J. C. Slater and G. F. Koster. *Phys. Rev.*, 94,1498, (1954).
- [5] K. Lendi. *Phys. Rev.*, B9,2433, (1974).
- [6] R. R. Sharma. *Phys. Rev.*, B19,2813, (1979).
- [7] K. Takegahara, Y. Aoki, and A. Yanase. *Journal of Physics C: Solid State Physics*, 13(4):583, 1980.
- [8] A. V. Podolskiy and P. Vogl. *Phys. Rev.*, B69,233101, (2004).
- [9] D. A. Papaconstantopoulos and M. J. Mehl. *Journal of Physics: Condensed Matter*, 15,R413, (2003).
- [10] M. J. Mehl and D. A. Papaconstantopoulos. *Phys. Rev.*, B54,4519, (1996).
- [11] M. D. Jones and R. C. Albers. *Phys. Rev.*, B66,134105, (2002).
- [12] M. D. Jones and R. C. Albers. *Phys. Rev.*, B79,045107, (2009).
- [13] D. A. Papaconstantopoulos. *Handbook of the Band Structure of Elemental Solids*. 2nd Edition, Springer, (2014).
- [14] M. J. Mehl, B. M. Klein, and D. A. Papaconstantopoulos. In J. H. Westbrook and R. L. Fleischer, editors, *Intermetallic Compounds: Principles and Applications*, volume 1. Wiley, London, 1994.
- [15] R. A. Reese, S. K. Sinha, and D. T. Peterson. *Phys. Rev.*, B8,1332, (1973).
- [16] A. Ghorai and S. K. Sen. *Phys. Stat. Sol.*, B139,77, (1987).
- [17] L. W. Nixon and D.A. Papaconstantopoulos. *Physica C: Superconductivity*, 470(1718):709 – 715, 2010.
- [18] L. W. Nixon, D. A. Papaconstantopoulos, and M. J. Mehl. *Phys. Rev. B*, 78:214510, Dec 2008.
- [19] F. Herman and S. Skillman. *Atomic Structure Calculations*. Prentice Hall, Inc, (1963).