Block-Diagonalization and f-electron Effects in Tight-Binding Theory

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(Dated: March 22, 2002)

We extend a tight-binding total energy method to include \( f \)-electrons, and apply it to the study of the structural and elastic properties of a range of elements from Be to U. We find that the tight-binding parameters are as accurate and transferable for \( f \)-electron systems as they are for \( d \)-electron systems. In both cases we have found it essential to take great care in constraining the fitting procedure by using a block-diagonalization procedure, which we describe in detail.

PACS numbers: PACS numbers: 71.15.Ap, 71.15.Nc, 71.20.Gj

I. INTRODUCTION

In order to use atomistic modeling to predict materials properties it is necessary to accurately determine the forces between the atoms in a solid. Most of the established molecular dynamics simulations involve either pair potentials, embedded-atom potentials, or, for covalent materials like Si, some classical potentials with additional bond-angle information. Unfortunately, these methods have often proved inadequate for complex transition-metal and \( f \)-electron systems, which have important bond-bending forces that seem difficult to capture in any simple way. A promising approach for such systems is tight-binding (TB), since it automatically builds in the quantum-mechanical bonding that conventional first-principles local-density approximation (LDA) or gradient corrected (GGA) band-structure calculations can very accurately determine.

In this work we report on our progress to extend the recent TB total energy model that was developed at the U.S. Naval Research Laboratory (NRL); this has been successfully applied to semiconductors and both simple and transition metal \( d \)-electrons, and apply it to the study of \( f \)-electron systems as they are for \( d \)-electron systems. We have extended and tested the NRL-TB scheme to include \( f \)-electrons, which makes possible the exploration of materials with important \( f \) characteristics, such as the light actinides. We also describe our own specific methodology for our fitting procedures, which is based on the NRL procedures, that we believe should produce parameterizations that are highly accurate and should be well suited for molecular dynamics simulations, although we report no such simulations in this paper. In the rest of the paper, we first briefly recapitulate our modifications to the NRL approach, and describe our experience in obtaining high quality TB parameters. We test this approach for an s-p bonded material (Be), \( d \)-electron materials with nearly filled and partially filled \( d \)-bands (Cu and Nb), and finally for a partially filled \( f \)-band system (U), an element of significant technological importance, which has complex structural properties.

One of the major obstacles in atomistic methods for materials modeling is the question of transferability, which arises from the semi-empirical nature of the atomistic forces, which involve fitting parameters to either experimental data or to theoretical calculations. The problem of transferability is the question of how well such fitting parameters will work for geometries of atoms that are different from those to which they were fit. This question is especially important for molecular dynamics simulations, where the atoms are free to move wherever the atomic forces push them. It is also needed for determining ground-state structures — the structure that will minimize the total energy of the system — or for calculating various defect structure (vacancies, interstitials, and more complex defects) that are expensive for first-principles methods (LDA calculations). In this paper we will show that the TB method works for a wide variety of different atomic environments (e.g., for crystal structures with very different numbers of near neighbors) and over a large atomic volume range.

Another qualitative feature of atomistic potentials that is required for accurate molecular dynamics and other atomistic simulations is to parameterize self-consistency or local environmental effects. To understand what we mean by this statement, consider first-principles electronic-structure calculations for the total energy of a solid as a function of the atomic positions. Such calculations depend on determining a self-consistent potential for the electrons for every atomic structure considered. An electronic potential for any given atom depends importantly on the local arrangement of nearby atoms. This implies that any force parameterization that successfully mimics the electronic-structure calculation also senses changes in the local atomic environments. This concept has been a major driving force for adding local environmentally sensitive terms in atomic force models. The NRL-TB parameterization also contains such effects for onsite terms (see below). One strong test of local atomic rearrangements is the number of near-neighbors, which should strongly perturb the local charge.
density around any given atom and hence exacerbate self-consistency effects. For this reason we have focused our fitting procedures for TB parameters on crystal structures with widely varying numbers of nearest neighbors. As we will describe below, the NRL parameterization appears to have adequate flexibility to successfully pass this fairly stringent test.

All empirical force models use some procedure to fit their parameters (usually some variation on a least-squares fit to either experimental or theoretical data). As more parameters are added, perhaps to better describe bond-bending forces or approximate environmental effects, overall properties such as the total energy often become less sensitive to the parameters. What is actually worse is that different parameters can sometimes compensate for each other so that parameter space becomes a vast multidimensional landscape where the minimizing function often has large numbers of weak minima and it is difficult to find the physically relevant true global minimum that provides maximum transferability. Since it is difficult to find the physically relevant true global minimum, it is often a choice of different parameterizations, it rests upon the division of the total energy of the system into a repulsive pairwise term and contributions from the valence band structure,

\[ E_T = E_{\text{rep}} + E_b, \]

itself an approximation to the Harris-Foulkes functional, which can be derived from Kohn-Sham density functional theory (DFT),

\[ \mathcal{E}[n] = \sum_{i,v} \epsilon_{i,v} - E_H[n_v] - \int n_v(\epsilon_{xc}[n_v]) - V_{xc}[n_v]) + \frac{1}{2} \sum_a \sum_{b \neq a} Z_{va}Z_{vb}/|\mathbf{R}_a - \mathbf{R}_b|. \]

In our TB fits, we have found it to be enormously important to add constraints to the fitting procedure in order to force the parameters to be near the physically relevant portion of parameter space. Once this is done, any minimization procedure seems to improve the minimizing function as well as the transferability. Using physically motivated constraints appears to remove the huge degeneracy of multiply compensating parameters and to help focus the parameterization onto the desired solution. In the case of TB, as we will discuss below, the key constraint is symmetry. If used properly, it appears to force parameter space into highly transferable parameterizations.

II. TB METHOD

Theoretical justification for the tight binding method rests upon the division of the total energy of the system into a repulsive pairwise term and contributions from the valence band structure,}

\[ H_{\alpha i, \beta j} = \left\langle \alpha, i \right| -\nabla^2 + \sum_k V_{\alpha i}^{\text{eff}} \left| \beta, j \right\rangle, \]

the Hamiltonian including the labels for orbitals having generic quantum numbers \( \alpha, \beta \) localized on atoms \( i, j \), where the effective potential is assumed to be spherical, and can be represented as a sum over atomic centers,

\[ H_{\alpha i, \beta j} = c_\alpha \delta_{\alpha \beta} \delta_{ij} + E_{\alpha i, \beta j}(1 - \delta_{ij}), \]

for the single particle eigenvalues and orbitals, under the restrictions: terms involving more than two centers are ignored, terms where the orbitals are on the same atomic site are taken as constants, and the resulting reduced set of matrix elements are treated as variable parameters. Note that Eq. 3 includes the overlap matrix, \( S \), to take into account that the basis functions need not be orthogonal. To better illustrate these restrictions, we write

In Eq. 2, the subscript \( v \) denotes the fact that we are dealing only with the valence electrons whose density is given by \( n_v \), and the first term on the right hand side is the band term - a sum over eigenvalues arising from a Schrödinger-like equation. \( E_H \) denotes the Hartree energy, and \( \epsilon_{xc} \) and \( V_{xc} \) the exchange and correlation energy and potential, respectively. A simple decomposition of this functional into pairwise and bonding terms (Eq. 1) can be justified when terms involving more than two atomic centers are ignored (see Eq. 3 below), and the input charge density is atomic-like. The Slater-Koster method then consists of solving the secular equation,
where the on-site terms, \( e_\alpha \), represent terms in which two orbitals share the same atomic site, and, for \( j \neq i \),

\[
E_{\alpha i, \beta j} = \sum_n e^{i k (R_n + b_j - b_i)} \times \int d\mathbf{r}_\alpha (\mathbf{r} - \mathbf{R}_n - \mathbf{b}_i) \mathbf{H} \psi_\beta (\mathbf{r} - \mathbf{b}_j),
\]

(6)

\[
S_{\alpha i, \beta j} = \sum_n e^{i k (R_n + b_j - b_i)} \times \int d\mathbf{r}_\alpha (\mathbf{r} - \mathbf{R}_n - \mathbf{b}_i) \psi_\beta (\mathbf{r} - \mathbf{b}_j),
\]

(7)

are the remaining energy integrals involving orbitals located on different atomic sites. In Eqs. (6) and (7) we have used translational invariance to reduce the number of sums over bravais lattice points \( \{ R_n \} \), and the \( b_i \) denote atomic basis vectors within the repeated lattice cells. Orthogonal TB (OTB) treatments do not use Eq. (6), and thus have fewer parameters, but we have found a non-orthogonal (NOTB) approach to be more accurate, consistent with previous TB work. All of the results that we report in this paper use a NOTB model. Note that terms which have both orbitals located on the same site, but the potential on other sites have been ignored - these contributions are typically taken to be “environment” corrections to the on-site terms, and are not accounted for in the usual Slater-Koster formalism (although such corrections have been explored, for example, see Ref. 11 and references therein). The two center approximation then consists of ignoring additional terms in the inter-site contributions in which the effective potential does not lie on one of the atomic sites. This approximation is not necessarily very accurate (see, for example, the comparison between two and three-center fits in Ref. 4), but it is quite often used due to the enormous simplification of the overall TB method: perhaps one can view TB as having the right functional form and the choice of parameters allow some correction for any errors due to neglected terms. Once this approximation has been made, well justified or not, the inter-atomic (\( i \neq j \)) matrix elements reduce to a simple sum over angular functions and functions which depend only upon the magnitude of the distances between atoms,

\[
H_{\alpha i, \beta j} = \sum m h_{\ell m}(r_{ij}) G_{\ell m}(\Omega_{i,j}),
\]

(8)

\[
S_{\alpha i, \beta j} = \sum m s_{\ell m}(r_{ij}) G_{\ell m}(\Omega_{i,j}),
\]

(9)

where we have now adopted the usual convention of using the familiar \( \ell, m \) angular momentum quantum numbers, and the axis connecting the atoms is the quantization axis. The basis set used for the \( \alpha \) and \( \beta \) quantum states are the cubic harmonics whose functional forms are given by (with appropriate normalization factors)

\[
s_{\pm} = \sqrt{1/4\pi} |\pm\rangle,
\]

\[
p_{\pm} = \sqrt{3/4\pi} f_p(r)|\pm\rangle,
\]

\[
p_{2\pm} = \sqrt{3/4\pi} f_p(r) y_{2\pm}|\pm\rangle,
\]

\[
p_{3\pm} = \sqrt{3/4\pi} f_p(r) \bar{z}_{3\pm}|\pm\rangle,
\]

\[
|d_1\rangle = \sqrt{5/16\pi} f_d(r)(x^2 - y^2)|\pm\rangle,
\]

\[
|d_2\rangle = \sqrt{5/16\pi} f_d(r) y_{2\pm}|\pm\rangle,
\]

\[
|d_3\rangle = \sqrt{5/16\pi} f_d(r)(3z^2 - r^2)|\pm\rangle,
\]

\[
|f_1\rangle = \sqrt{7/16\pi} f_f(r)(x^2 - 3y^2)|\pm\rangle,
\]

\[
|f_2\rangle = \sqrt{7/16\pi} f_f(r)(y^2 - 3z^2)|\pm\rangle,
\]

\[
|f_3\rangle = \sqrt{7/16\pi} f_f(r) y(z^2 - x^2)|\pm\rangle,
\]

\[
|f_4\rangle = \sqrt{7/16\pi} f_f(r)(z^2 - 3x^2)|\pm\rangle,
\]

\[
|f_5\rangle = \sqrt{7/16\pi} f_f(r)(z^2 - x^2)|\pm\rangle,
\]

\[
|f_6\rangle = \sqrt{7/16\pi} f_f(r)(z^2 - y^2)|\pm\rangle,
\]

\[
|f_7\rangle = \sqrt{7/16\pi} f_f(r)(z^2 - y^2)|\pm\rangle,
\]

where \( f_p(r) = 1/r^l \), and \( |\pm\rangle \) denotes the spin-state. The selection of these particular functions is not accidental, as they are chosen to specifically possess the various irreducible representations of the cubic point group \( O_h \). In principle we are free to choose any set of orthogonal functions as our basis, but it is beneficial to choose the set that best reflects the symmetry properties of the system under study. Other choices exist, but they do not provide nearly as transparent a framework for modeling, fitting and understanding the various parameters.

The Slater-Koster tables for the \( s^{10}d^5 \) matrix elements can be found in standard references, and we have used the tabulated results of Takegahara et al. for the additional matrix elements involving \( f \)-electrons. Typical TB applications are then reduced to using TB as an interpolation scheme; the matrix elements \( h_{\ell m}, s_{\ell m} \) (if used) and \( e_\alpha \) are determined by fitting to \textit{ab-initio} calculated quantities such as the total energy and band energies. The NRL-TB total energy method was an innovation in that the energy bands used in the TB fits were shifted such that the integrated band energy was the total energy,

\[
e_b = (E_b + E_{tot})/N_v,
\]

(10)

where \( e_b \) are the unshifted energy band values, \( E_b = \sum \epsilon_\alpha \) the total band energy, and \( E_{tot} \) the computed total energy. The NRL-TB method imposes a simple functional form on the inter-site matrix elements,

\[
h_{\ell m}(r) = (a_{\ell m} + b_{\ell m} r) e^{\exp(-c_{\ell m} r) f_c(r)},
\]

(11)

\[
s_{\ell m}(r) = (a_{\ell m} + b_{\ell m} r) e^{\exp(-c_{\ell m} r) f_c(r)},
\]

(12)

where \( f_c = 1/(1 + \exp(2*(r - r_0))) \) is a multiplicative factor included to ensure a smooth cutoff with increasing distance. Our applications have used \( r_0 = 13.5 \) bohr radii for Cu and Nb, \( r_0 = 10 \) for Be, and \( r_0 = 12.0 \) for U. The on-site terms include the environment dependence
the usual NRL-TB approach

\[ e_α = e_α^0 + e_α^1 ρ^{2/3} + e_α^2 ρ^{4/3} + e_α^3 ρ^2. \]  

(13)

The \( ρ \) function is intended to be a crude measure of the atomic density (providing a correlation to the number of atomic neighbors),

\[ ρ = \sum_{i≠j} \exp (-\lambda^2 r_{ij}) f_c(r_{ij}), \]  

(14)

where \( r_{ij} \) is the interatomic distance. Note that, for a NOTB model in our \( sp^3df^7 \) basis, this TB model has \( 1 + 16 + 2 \times (3 \times 20) = 137 \) free parameters, whose determination is the key to an accurate representation.

| \( p \) | \( f \) |
|---|---|
| 1 | \( \{ |a\rangle, \{d_5\} \} \) |
| 2 | \( \{ |d_4\} \) |
| 3 | \( \{ |f_1\} \) |
| 4 | \( \{ |d_1\} \) |
| 5 | \( \{ |f_2\} \) |
| 6 | \( \{ |p_3\}, \{f_4\} \) |
| 7 | \( \{ (|p_2| + |p_1|)/\sqrt{2} \} \) |
| 8 | \( \{ |p_1\}, \{f_3\}, \{f_5\} \} \) |

TABLE I: Basis functions used in the block-diagonalization of high-symmetry point \( X \) in the fcc lattice. Only one of the two partners is shown for the two-dimensional representations.

A. Fitting the Parameters

In order to determine such a large set of parameters, the usual NRL-TB approach involves performing a non-linear least squares minimization, fitting to the energy bands and total energies calculated from density functional theory. The energy bands are fitted over a set of points in the irreducible wedge of the first Brillouin zone (IBZ). In practice we have found it absolutely necessary to take maximum advantage of the symmetry present in order to impose constraints on the fitting process. We exploit the symmetry of all possible high-symmetry points and lines in the first Brillouin zone in order to reduce the possibility that the fitting process can easily mistake the ordering of the energy bands. We have decomposed the TB wavefunction at each high symmetry point and line in terms of the symmetry-adapted TB basis functions, which allows us to block-diagonalize the Hamiltonian and overlap matrices, and determine the eigenvalues corresponding to each irreducible representation, which avoids possible confusion as to the band ordering. This process is illustrated schematically by Figure 1. Figure 2 shows the perils of fitting using a simple energy ordering scheme for the bands - unless the irreducible representation is identified and constrained for each band, the actual fitting errors are misidentified.

Let us describe the scheme mathematically and follow up with a simple example. Along symmetry lines and planes in the Brillouin zone, there exist symmetry operations for each \( k \) that form a group. For each such group the irreducible representations \( \Gamma^p \) can be found, and can be used to block-diagonalize the secular equation,

\[ D(p)_{ij} = \langle \phi_j^p | H | \phi_i^p \rangle - E \langle \phi_j^p | \phi_i^p \rangle, \]  

(15)

where \( D(p) \) now takes on the “block-form”, and the symmetry reduced eigenvalues can be found by solving

\[
\begin{bmatrix}
D(1) & 0 & 0 & \ldots \\
0 & D(2) & 0 & \ldots \\
0 & 0 & D(3) & \ldots \\
\vdots & \vdots & \vdots \\
\end{bmatrix} = 0,
\]  

(16)

or simply \( |D(p)| = 0 \) for every \( p \).

The resulting set of symmetry adapted basis functions are specific linear combinations of the original cubic harmonic basis functions (Eq. 1), which can be found, in practical terms, by applying projection operators of the irreducible representations to the original basis functions. In our fits, we require that only the correct symmetry adapted tight-binding basis functions can be used for fitting each energy eigenvalue for high symmetry \( k \) points and directions in the Brillouin zones for the various cubic crystal structures. In this way we fit not only the energy eigenvalues, but also we restrict the eigenfunctions as well. One must then also provide the TB fit with a database in which the energy bands are broken down by their irreducible representation at each high symmetry point and direction. In practice this means that the linear combinations of TB basis functions that have the irreducible representations at each \( k \) must be determined. These linear combinations then “block-diagonalize” the Hamiltonian and overlap matrices as described above.

The use of symmetry in constraining the fitting process has previously been developed by Papaconstantopoulos for \( sp^3df^7 \) basis. We have found our procedure for using symmetry constraints to be essential in limiting the
parametric phase space and thereby obtaining transferable TB parameters. Here we extend the scheme to include $f$-electrons. We wish to strongly emphasize how important this procedure has been in determining an accurate fit, especially with the large parameter set used when fitting to an $sp^d$ basis. As an example, in the fcc lattice structure, each energy band at the point X [with cartesian coordinates $(0, 2\pi/a, 0)$] can be decomposed into different symmetry-adapted combinations of the basis functions, as shown in Table I, where we have included, for the two-dimensional representations $E_g$ and $E_u$, only one of the two possible partners. Note that we are thus able to essentially fit the eigenfunctions as well as the eigenvalues by this use of the block-diagonalization procedure. In the above listing, the first column is simply the conventional band label, the second the conventional group symbol ($g$ and $u$ are the usual positive and negative parity labels), and the third column lists the basis expansion functions belonging to that particular irreducible representation.

To begin the fitting procedure, it is necessary to make some choice of initial parameters. In our experience, the fitting procedure was not sensitive to the choice of initial parameters, provided that the block-diagonalization procedure was used as the fit was optimized.

For this reason, we have typically chosen a very simple initial set of parameters. We usually set $\lambda = 1$, $e_{p_i}^0$ near the expected center of the relevant band and the other $e_{p_i}^0 = 0$ for $i = 1, 2, 3$, and the diagonal elements of $s = 1$. All of the off-diagonal elements for both the Hamiltonian and overlap matrices are started at zero. With this starting set, we typically optimize one of the cubic structures for 3 or 4 volumes spanning the range of volumes of interest, and allow the parameters to optimize with block-diagonalization. This provides the real starting TB parameters.

The fitting process involves standard nonlinear least squares algorithms. Because this type of optimization process is prone to becoming trapped in local minima, the initial step described is important in order to provide a good starting point for the full fitting process.

An alternative starting procedure has been described by NRL, which involves algebraically solving a simplified nearest-neighbor tight-binding model at high symmetry points for cubic crystal structures and then comparing the solution to the LAPW bands at the specified points to determine a resulting reduced set of parameters. These are then used as the starting values for the nearest-neighbor-shell non-hybridizing matrix elements, namely \{ss, pp, pp, dd, dd, dd, ff, ff, ff, ff, ff\}. Other matrix elements are started with zero value. We have also tried this, more complicated, procedure. However, we converged to fits of comparable quality as our standard approach (described above).

In the full optimization we include fcc, bcc, and sc crystal structures in addition to the ground-state crystal structure (if different) and any other structures of interest. Because we know the correct block-diagonalization at high symmetry points and lines for the cubic phases, keeping these in the fit prevents the minimization from wandering into unphysical parts of parameter space. For all structures and volumes included in the fit, we use both the energy eigenvalues of the relevant bands as well as the total energy. During the minimization procedure, we typically weight the total energies by a factor of 1,000 to 10,000 times that of individual energy eigenvalues, and include a penalty factor for singular overlap matrices. No block-diagonalization was done for the non-cubic structures.

### B. The Database

To determine the TB parameters, we have fit to a database of highly accurate total energies and energy bands from a series of full-potential linearized augmented plane-wave (FLAPW) calculations including local orbitals. The data for which each element was fit consisted of energy bands and total energies for a series of volumes in various crystal structures. Table II lists the number of volumes and crystal structure types for each of the elements studied here, Be, Cu, Nb, and U. Also shown in Table II is the number of energy bands fit in each volume, $N_b$, and the number of volumes fit in each crystal structure, $N_V$. Also listed are the average root-mean-square errors in the fitted energy bands, $(\epsilon_s)$, and the average error in the fitted total energy, $\langle E_T \rangle$.

| Element | Structure | $N_V$ | $N_b$ | $\langle \epsilon_s \rangle$ [eV] | $\langle E_T \rangle$ [eV] |
|---------|-----------|-------|-------|-------------------------------|---------------------------|
| Be      | fcc       | 9     | 3     | 0.73                          | 0.0063                    |
|         | bcc       | 7     | 3     | 0.69                          | 0.0053                    |
|         | sc        | 6     | 3     | 1.01                          | 0.0034                    |
| Cu      | fcc       | 12    | 6     | 0.11                          | 0.0018                    |
|         | bcc       | 8     | 6     | 0.12                          | 0.0021                    |
|         | sc        | 9     | 6     | 0.12                          | 0.0027                    |
| Nb      | fcc       | 7     | 6     | 0.25                          | 0.0021                    |
|         | bcc       | 8     | 6     | 0.25                          | 0.0018                    |
|         | sc        | 5     | 6     | 0.29                          | 0.0015                    |
| U       | fcc       | 6     | 9     | 0.42                          | 0.0105                    |
|         | bcc       | 5     | 9     | 0.36                          | 0.0075                    |
|         | sc        | 6     | 9     | 0.59                          | 0.0082                    |
|         | oC4       | 14    | 18    | 0.39                          | 0.0173                    |

To conclude, we have identified a database of highly accurate total energies and energy bands from a series of full-potential linearized augmented plane-wave (FLAPW) calculations including local orbitals. The data for which each element was fit consisted of energy bands and total energies for a series of volumes in various crystal structures. Table II lists the number of volumes and crystal structure types for each of the elements studied here, Be, Cu, Nb, and U. Also shown in Table II is the number of energy bands fit for k-points in the IBZ, 47 IBZ k-points were used for fcc and bcc lattices, 56 for sc, and 24 for α-U, which were also used in determining the total energies using a temperature broadening special point integration (using a broadening of 2mRy). The block diagonalization procedure was carried out at all high-symmetry points as well as the midpoints of all high symmetry directions in the IBZ, which made it necessary to break down the FLAPW energy bands by their irreducible representation at all such points. A representative plot illustrating the quality of the TB fit for low lying energy bands is shown in Figure IIB, in this case for fcc U near the equilibrium.
volume; note that we show bands for the fcc structure rather than the ground-state structure in order to reduce the complexity of the figure (a similar figure for α-U would have 2 times as many bands). The fit quality is quite good for a substantial energy region extending far above the fermi level. The highest energy bands involve higher-lying orbitals that are not included in our tight-binding basis, and hence the TB fit breaks down at high energy. For one crystal structure it is often possible to fit the energy bands so well that the difference between the LAPW and the TB bands are almost indistinguishable. However, when all of the different structures are added into the TB fitting procedure, the overall quality of the fit to the individual energy bands tends to degrade to that shown in Figure II B. In practice, we have found that improving the total energy fit lower than 1 mRy requires some compensating increase in the individual energy band errors. Ideally the two sets of errors should collectively decrease (after all, the total energy is the sum of the occupied band energies), but there may be some shortcoming in the functional form of the TB parameters that cause the two sets of errors to compensate for one another rather than for them to behave collectively. We hope to explore this issue in future work by considering alternate functional forms.

These FLAPW results matched very well with a recent \textit{ab-initio} study of the structural properties of U using FLAPW and a complementary technique using a basis set of Gaussian type orbitals\cite{19}. We have neglected spin-orbit coupling for U, which has little effect on the bulk properties\cite{20}. In a future paper we will extend this TB technique to include spin orbit coupling for f-electron materials (application to a three center \textit{sp}^3 basis has been explored, for example, in Ref\cite{21}), and apply it to heavy elements.

III. APPLICATION TO METALLIC ELEMENTS

We now apply the TB total energy method to a range metallic elements from the periodic table. In order to provide a fair test for the TB method as an interpolation scheme, we have selected Be to represent light metals, Cu and Nb for transition metals, and U as a heavy f-electron metal. Table III list the structural properties predicted by our TB fits, compared with FLAPW and experimental results. In general, the TB fits are very accurate, and highly transferable. The equilibrium volume, \(v_0\), and bulk modulus, \(B_0\), as well as the pressure derivative of the bulk modulus, \(B'_0\), were determined by fitting the various equation of state curves to a second order Birch equation of state\cite{30}.

\textit{Beryllium.} The alkaline-earth metal Be belongs to a part of the periodic table known for nearly free electron behavior, yet the properties of this metal, including the \(c/a\) ratio, are strongly influenced by the directional character of the interatomic bonding. In determining our TB fit for Be, we used a \textit{sp}^3\textit{d}^5 basis with parameters fit to a database of 22 different volumes in the fcc, bcc, and sc phases. It was necessary to restrict the fit to only the three lowest energy valence bands (\(N_V\) in Table II) for Be, as the bands corresponding to the atomic 3s states lie just above the fermi level, and our basis set has only a single s-type basis function (a fit using an additional s state would be able to fit higher energy bands). We found that an accurate model required inclusion of the \(d\) orbitals, which are quite close energetically to the occupied
TABLE III: Structural parameters of hcp Be, fcc Cu, bcc Nb, and α-U in the TB model, FLAPW calculation, and experiment (at a temperature where consistent structural and elastic data was available, noted in parentheses). The equilibrium volume is denoted by $v_0$, and the bulk modulus and its pressure derivative by $B_0$ and $B_0'$. $y$ is the atomic position parameter in the $oC4$ $α$-U structure.

| method          | $v_0$ ($\text{Å}^3$) | $B_0$ (GPa) | $B_0'$ | $c/a$ | $b/a$ | $y$ |
|-----------------|----------------------|-------------|--------|-------|-------|-----|
| hcp Be          |                      |             |        |       |       |     |
| TB              | 8.04                 | 127         | 2.0    | 1.565 |       |     |
| FLAPW           | 7.90                 | 123         | 3.33   | 1.553 |       |     |
| Expt(100K)$^a$  | 8.05                 | 115$^b$     |        | 1.571 |       |     |
| fcc Cu          |                      |             |        |       |       |     |
| TB              | 11.9                 | 139.0       | 5.1    |       |       |     |
| FLAPW           | 11.9                 | 140.3       | 5.1    |       |       |     |
| Expt(293K)$^c$  | 11.79$^d$            | 138         | 5.3    |       |       |     |
| bcc Nb          |                      |             |        |       |       |     |
| TB              | 18.1                 | 160         | 3.9    |       |       |     |
| FLAPW           | 18.1                 | 161         | 3.8    |       |       |     |
| Expt(120K)$^e$  | 18.02$^f$            | 171.6$^g$   |        |       |       |     |
| α-U             |                      |             |        |       |       |     |
| TB              | 20.24                | 131         | 2.8    | 1.732 | 2.044 | 0.1017 |
| FLAPW           | 20.14                | 142         | 5.0    | 1.741 | 2.073 | 0.0990 |
| Expt$^g$        | 20.58                | 136$^h$     | 1.734  | 2.063 | 0.1023 |  

$^a$Ref. 22  
$^b$Ref. 23  
$^c$Ref. 24  
$^d$Ref. 25  
$^e$Ref. 26  
$^f$Ref. 27  
$^g$Ref. 28  
$^h$Ref. 29

s and p orbitals. The ground state structural parameters for the Be TB model are compared with experiment in Table III. Figure 3 shows that our TB model successfully predicts the ground state crystal structure (hcp) in addition to an accurate prediction of the equilibrium volume and $c/a$ ratio. The $c/a$ ratio was determined by using a cubic polynomial fit to total energy calculations for 8 $c/a$ values around the experimental value.

Copper and Niobium. Equation of state plots comparing our TB model for the transition metals Cu and Nb are shown in Figures 4 and 5. The predicted structural parameters are given in Table III. For both transition metals the lowest six energy bands were fitted throughout the IBZ. For both elements the ground state structure is cubic, with a small energy difference between the face and body-centered structures, which the TB fit reproduces quite well. Note the excellent agreement between the TB model and the FLAPW calculations, as well as the broad range of volumes and energies fitted.

Uranium. For U, it has been shown that the bulk structural properties are rather insensitive to the treatment of spin-orbit coupling for the valence electrons$^{20}$, so this element makes a good test case for the scalar relativistic treatment that we have thus far implemented in our TB method. For U, the lowest 9 energy bands per atom were fit throughout the IBZ for the cubic crystal structures as well as the $α$-U structure ($oC4$). The atomic position parameter, $y$, was determined by performing a cubic fit to a six calculations of the total energy versus $y$. The ratios $b/a$ and $c/a$ were then found by using this value of $y$ and performing a set of total energy calculations at the experimental volume for twenty values of $b/a$ and $c/a$. The ratios that minimized the total energy were then found using a 10 parameter, two dimensional cubic polynomial. The equation of state for the $α$, fcc, bcc, and sc phases are shown in Figure 6 which shows excellent agreement

FIG. 4: Equation of state curves for various crystal phases of Cu, both in TB (solid symbols), and in FLAPW (solid curves).
FIG. 5: Equation of state curves for various crystal phases of Nb, both in TB (solid symbols), and in FLAPW (solid curves).

between the calculated total energies between FLAPW and TB, thus justifying TB as an accurate interpolation scheme, even for f-electron materials. Again the agreement between the TB and FLAPW calculations is excellent.

FIG. 6: Equation of state curves for various crystal phases of U, both in TB (solid symbols), and in FLAPW (solid curves).

IV. CONCLUSIONS

We have presented the results of a study of the structural properties of the metallic elements Be, Cu, Nb, and U using a tight-binding total energy method. Fits for the TB method were obtained from highly accurate FLAPW calculations. The TB models thus derived are highly efficient, due to the treatment of valence electrons only, and highly accurate, proving to be transferable to new structures not included in the original fit.

We have also shown that the NRL total energy tight-binding parameterization is highly accurate for f-electron as well as for d-electron systems. In addition we have demonstrated that forcing the tight-binding fitting procedure to use the correct wave-function symmetry when fitting to specific energy eigenvalues at high symmetry k points and lines in the Brillouin zone leads to highly transferable tight-binding parameterizations. This parameterization seems insensitive to the initial guess used to start the least-squares minimization procedure.

Transferability is a key issue: do the tight-binding calculations accurately reproduce what a high-quality first-principles method would calculate? Like the answer for any approximation, our conclusions are mixed. The results of this paper show that the current NRL parameterization make it possible to fit the total energy as a function of volume (for a significantly large range of volumes) for many different crystal structures. This is a very significant degree of transferability.

With respect to other properties, additional detailed results will be published in future publications for applications to specific materials. However, it is possible and relevant to make some pertinent observations here. Like any large parameterization, the properties that can be accurately calculated depend on how well one has sampled all aspects of the parameterizations in the data base used to fit the parameters. Because of the highly complex and nonlinear relationship between the parameters and the properties, it is always difficult to guess ahead of time how well one has sampled the full parameter space. If the relevant sampling has been done well for the properties of interest, those properties will be accurately predicted and compare well with first-principles calculations for the same properties.

Some preliminary results indicate that elastic constants often are of about 10-20% accuracy. Transferability can be improved by specifically including in the fit finite distortions of the unit cell that sample those elastic constants (the distortions should be large enough to give a significant energy difference on the order of the difference between other crystal structures like fcc and bcc, yet small enough so that the energy change is quadratic in energy with the size of the distortion so that one remains in the elastic regime). Similarly, preliminary phonon calculations are of a similar degree of accuracy without any additional fine tuning of the parameters, but can be significantly improved by adding in a few frozen phonons of finite amplitude into the fit.

In addition, it is worth pointing out that adding in the diamond lattice into the fits seems to improve the phonons all by itself (before adding in frozen phonons, for example). The diamond lattice seems to sample other parts of the parameterization that have not been sampled...
by the other cubic crystal structures (e.g., with only four nearest-neighbors, it improves the sample of Eq. (15) to smaller \( \rho \)). As more experience is gained, it may be possible to find other crystal structures or other properties to include in the fits that similarly improve transferability. This is an ongoing work.

Finally, the NRL parameterization is certainly not the only possible parameterization. Significant improvement of transferability may be achieved by finding better functional forms for the hopping, overlap, and diagonal matrix elements.

For \( f \)-electron systems, because the rare-earth series of elements have localized \( f \) electrons (beyond Ce), the interesting systems are the actinide series. For this series it will be important to include spin-orbit coupling due to the large charge of the nucleus, especially for Np and Pu. We hope to explore addition of spin-orbit coupling to the tight-binding method for \( f \)-electron materials in future work.

To conclude: based on the excellent results of the tight-binding total energies that we have found for a wide variety of single-element metals and crystal structures, the tight-binding approach appears promising for providing highly accurate calculations of complicated geometries such as defect states and distorted structures, where many atoms are required in large supercells, and first-principles methods are prohibitively expensive.

Acknowledgments

All FLAPW calculations were performed using the Wien97 package. This research is supported by the Department of Energy under contract W-7405-ENG-36. Calculations were performed at the Los Alamos National Laboratory, the Center for Computational Research at SUNY–Buffalo, and the National Energy Research Scientific Computing Center (NERSC), which is supported by the Office of Science of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.