

Generalized Slater-Koster method for fitting band structures

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Abstract

A tight-binding procedure is presented for fitting electronic band structures of crystals. It is based on a fully automated method of determining all possible independent matrix elements for arbitrary crystal structures. A fit, using this method, for the band structure of hexagonal close-packed Tc is more than an order of magnitude better than previous fits. A practical procedure for optimizing fits is described. (A shortened version of this paper has been published in Physical Review B.)

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I. INTRODUCTION

The 1954 paper by Slater and Koster¹ established parameterized tight-binding as a method for fitting electronic band structures of crystals. In this method, matrix elements between atomic-like orbitals are treated as “disposable constants” with which to fit band structures calculated using some more accurate technique. This method has become quite widely used. Because it is an extremely fast technique, it has been applied to computationally intensive problems where many electron states are required, such as calculating electron-phonon interactions.² It is used extensively to study the electronic structure of semiconductor and metallic multilayers, alloys, and other disordered systems. Recently it has been used to parameterize total-energy calculations³ to enable calculations for extremely large systems.⁴

In their paper, Slater and Koster presented the so called two-center approximation for the matrix elements. This name derives from an approximation for the crystal potential as a sum of spherically symmetrical potentials around each atom. In this approximation, the matrix elements between orbitals on two different sites can involve the potential from either of the orbital sites, but not a third. Matrix elements which involve the potential from a third site are called three-center matrix elements, and are ignored in this approximation. The authors assert that, while these matrix elements are not negligible, they are ignored for convenience. For crystals with cubic symmetry only, they also worked out all of the independent matrix elements, including the three-center matrix elements. With these results they showed that, in fact, the three-center matrix elements can be important.

Besides neglecting the three-center matrix elements, the Slater-Koster two-center approximation differs from the full three-center formulation in that it reformulates the matrix elements. Instead of matrix elements between orbitals space quantized with respect to a particular direction in space it uses orbitals quantized with respect to the axis between them. In this case, the matrix elements are labeled as is common in molecular physics, $sp\sigma$, $pd\pi$, $dd\delta$, etc. This reformulation allows the automated calculation of the independent matrix

elements for arbitrary crystal structures,^{1,5} and is a major advantage of the Slater-Koster two-center approximation. On the other hand, calculations that use the three-center matrix elements can achieve better fits than those that use just the two-center matrix elements both because there are more fitting parameters available and because physically important matrix elements are neglected in the two-center approximation.

Until now, calculations using the three-center matrix elements have only been done for crystals with cubic symmetry, based on the work of Slater and Koster.¹ The set of independent matrix elements has been analyzed by group theoretical techniques,⁶ but these analyses have not lead to any practical fitting scheme.

In 1986, Papaconstantopoulos⁷ used the results of Slater and Koster and the non-orthogonal generalization of Mattheiss⁸ to generate a tabulation of high quality tight-binding fits to the band structures of many of the elements in the Periodic Table. This compilation has been quite widely used. For the face-centered cubic and body-centered cubic materials he considers, the best fits are found with the three-center formulation. For the hexagonal close-packed materials, he does not give a fit based on the three-center formulation, and the best fits for those materials are significantly worse than they are for the cubic materials. Since the slopes of the bands at the Fermi energy in *d*-band materials is often of the order of 0.1 eV/nm^{-1} , a root mean square error of 65 meV, typical of the best fits to the hexagonal close-packed materials, can lead to errors in the size of the Fermi surface of about 5-10% of distance to the zone boundary.

In this paper, I generalize the Slater-Koster two-center approximation to include the three-center matrix elements while retaining the reformulation in terms of orbitals space quantized with respect to the axis joining a pair of atoms. This approach allows the inclusion of the three-center parameters for fitting while retaining much of the ease of computation of the two-center approximation. I describe a way to completely automate, for arbitrary crystal structures, the determination of the independent matrix elements and the phase factors relating dependent matrix elements. I demonstrate the approach by determining the independent matrix elements for a series of crystal structures and then by showing fits to

band structure for a hexagonal-close-packed crystal.

This approach has been used to fit the band structures of a large number of transition metals.¹⁰ The fits were then used to determine the geometrical properties of the Fermi surfaces relevant to oscillatory exchange coupling in magnetic multilayers.¹⁰ For the face-centered-cubic and body-centered-cubic materials the fits were on average 25% better than those found by Papaconstantopoulos.⁷ This small difference is expected due to the equivalence of the fitting parameters for the cubic materials. For the hexagonal close-packed materials, on the other hand, the fits were better on average by roughly a factor of 20. This improved accuracy was crucial for accurate determination of the Fermi surface properties.

The main goal of the paper is to describe this method so that it can be used in much the same manner as methods based on the two-center approximation. Section II describes the method used to generate the three-center matrix elements. Section III describes the application of this method to fits of the band structures of three transition metals. Appendices A and B provide further details.

II. METHOD

Although the fitting procedure presented here is independent of approximations for the potential and the wave functions and depends only on the symmetry of the system, it is useful to think of the potential as a sum of spherically symmetrical potentials centered around each atom in the system. Wave functions are expanded around each atom, located at \mathbf{r}_j within the primitive unit cell, in terms of spherical harmonics, $Y_{\ell m}$, multiplied by radial wave functions. Each orbital is indexed by $L \equiv \{j, \ell, m\}$, the atomic site index j and the usual angular momentum indices, ℓ and m .

In developing this procedure, matrix elements will be divided into two types, matrix elements between orbitals on the same atomic site, on-site terms denoted by o , and matrix elements between orbitals on different atomic sites, bond terms denoted by b . The separations between atoms are described in terms of bonds b which are ordered pairs of atoms

within the unit cell or a neighboring one (via a lattice vector, \mathbf{R}), $b \equiv \{\mathbf{R}, j_{0b}, j_{1b}\}$. The bond vector, $\mathbf{R}_b = \mathbf{R} + \mathbf{r}_{j_1b} - \mathbf{r}_{j_0b}$, points from one atom to another, possibly in another unit cell. The set of bonds excludes those that couple an atom to itself, $\mathbf{R}_b = 0$.

In general, the Hamiltonian matrix can be written in terms of independent parameters, H_q and H_p , and structure factors, $S_{L,L'}^q$ and $S_{b,L,L'}^p$, as follows:

$$H_{L,L'}(\mathbf{k}) = \delta_{j,j'} \sum_q H_q S_{L,L'}^q + \sum_p H_p \sum_{b \in \{b_p\}} e^{i\mathbf{k} \cdot \mathbf{R}_b} S_{b,L,L'}^p, \quad (1)$$

Here q indexes parameters for on-site matrix elements and p indexes parameter for bond matrix elements. The sets of bonds, $\{b_p\}$, are the (equivalent) bonds, with which the parameter p is associated. Both the on-site structure factors, $S_{L,L'}^q$, and the bond structure factors, $S_{b,L,L'}^p$, are independent of the wave vector, \mathbf{k} , and the fitting parameters, H_p . The structure factors depend only on the crystal structure. Because the parameters are associated with specific angular momenta, most of them are zero.

To evaluate on-site structure factors, it is useful to expand the potential around each atom as a sum over all terms, indexed by ν , allowed by symmetry

$$V(\mathbf{r} + \mathbf{r}_j) = \sum_\nu V^\nu(r) \sum_{m=-\ell_\nu}^{\ell_\nu} C_{j,m}^\nu Y_{\ell_\nu m}(\hat{\mathbf{r}}). \quad (2)$$

The expansion of the potential and the derivation of the on-site structure factors is discussed in Appendix A. Each symmetry-allowed term is associated with a set of equivalent atomic sites, $\{j_\nu\}$. The on-site parameters are each associated with a symmetry-allowed term, ν_q , and two angular momenta, ℓ_q and ℓ'_q . For $j \in \{j_{\nu_q}\}$, $L = \{j, \ell_q, m\}$, and $L' = \{j, \ell_q, m'\}$ the structure factors are

$$S_{L,L'}^q = C_{j,(m-m')}^{\nu_q} G(\ell_q m, \ell_{\nu_q}(m - m'), \ell'_q m'), \quad (3)$$

where G is a Gaunt coefficient

$$G(\ell m, \ell''(m - m'), \ell' m') = \int d\Omega Y_{\ell m}^*(\hat{\mathbf{r}}) Y_{\ell''(m-m')}(\hat{\mathbf{r}}) Y_{\ell' m'}(\hat{\mathbf{r}}). \quad (4)$$

For all other values, the structures factors associated with the parameter q are zero. These on-site structure factors are of two types, one-center integrals and crystal-field integrals.

The one-center integrals are derived from the symmetry terms in Eq. (2) with $\ell_\nu = 0$, so that the one-center structure factors simplify to $S_{L,L'}^q = \delta_{\ell,\ell'}\delta_{m,m'}/\sqrt{4\pi}$. All of the other structure factors are called crystal-field integrals. When the potential is approximated by a sum of spherical potentials around each atom, these structure factors can be understood as coming from integrals between two orbitals centered on one site and a potential centered on a different site.

To find bond structure factors, it is useful to expand the potential around each bond as a sum over all terms allowed by symmetry

$$V(\phi, z, \rho) = \sum_m V_{b,|m|}(\rho, z) B_m^b e^{im\phi}, \quad (5)$$

where the coordinates, ρ , z , and ϕ , are defined around the bond. The expansion of the potential and derivation of bond structure factors are discussed in Appendix B. Each bond parameter is associated with a set of equivalent bonds $\{b_p\}$, a direction along those bonds, set by choosing one of the atoms, j_p , and several angular momenta, ℓ_p , ℓ'_p , m_p , and m'_p . A given set of bonds falls into one of two cases: either the two defining atoms for a bond are equivalent, or they are not. If they are equivalent, some symmetry operation of the crystal maps one atom into the other.

If a given set of bonds is symmetric, bond parameters for $L = \{j_{1p}, \ell_p, m_p\}$, $L' = \{j_{0p}, \ell'_p, m'_p\}$ and $L = \{j_{1p}, \ell'_p, m'_p\}$, $L' = \{j_{0p}, \ell_p, m_p\}$ are the same up to a sign. This sign is one except possibly when $m_p \neq m'_p$ because $V_{b,m}(\rho, z)$ can be odd with respect to inversion around the center of the bond and still satisfy the appropriate symmetries. This sign is defined to be σ_p . For $\ell_p = \ell'_p$ and $m_p = m'_p$ the two contributions are the same, and σ_p is defined to be zero. Combining the contributions for $L = \{j_{1p}, \ell_p, m\}$ and $L' = \{j_{0p}, \ell'_p, m'\}$, the bond structure factors are

$$\begin{aligned} S_{b,L,L'}^p = & \sum_{\sigma=\pm} (D_{\ell_p(\sigma m_p)m}^b)^* D_{\ell'_p(\sigma m'_p)m'}^b (-1)^{\ell_p - \sigma m_p} S_{\sigma m_p} S_{\sigma m'_p} B_{\sigma m_p - \sigma m'_p}^b \\ & + \sigma_p \sum_{\sigma=\pm} (D_{\ell'_p(\sigma m'_p)m}^b)^* D_{\ell_p(\sigma m_p)m'}^b (-1)^{\ell'_p - \sigma m'_p} S_{\sigma m'_p} S_{\sigma m_p} B_{\sigma m'_p - \sigma m_p}^b. \end{aligned} \quad (6)$$

$D_{\ell mm'}^b$ is the rotation matrix for spherical harmonics,¹⁴ for the rotation that brings each

bond into the z -direction by rotation perpendicular to both \hat{z} and \mathbf{R}_b . The sign, s_m , enters from the definition of spherical harmonics in terms of associated Legendre polynomials, $P_{\ell m}$,

$$s_m = \begin{cases} 1 & \text{if } m < 0 \\ (-1)^m & \text{if } m \geq 0 \end{cases}. \quad (7)$$

If a bond is asymmetric, rotating $\hat{\mathbf{r}}_{-b}$ into the z -direction does not give the same physical situation as rotating $\hat{\mathbf{r}}_b$ into the z -direction. For each set of equivalent asymmetric bonds, half do not give the same physical situation as the other half. In this case, half of the bonds are rotated into the the positive z -direction and the other half into the negative z -direction. For the half that are rotated into the positive z -direction and the orbitals $L = \{j_{1p}, \ell_p, m\}$ and $L' = \{j_{0p}, \ell'_p, m'\}$, the structure factors are

$$S_{b,L,L'}^p = \sum_{\sigma=\pm} (D_{\ell_p(\sigma m_p)m}^b)^* D_{\ell'_p(\sigma m'_p)m'}^b (-1)^{\ell_p - \sigma m_p} s_{\sigma m_p} s_{\sigma m'_p} B_{\sigma m_p - \sigma m'_p}^b. \quad (8)$$

For the other half of the bonds and the orbitals $L = \{j_{0p}, \ell'_p, m'\}$ and $L' = \{j_{1p}, \ell_p, m\}$, the structure factors are

$$S_{b,L,L'}^p = \sum_{\sigma=\pm} (D_{\ell'_p(\sigma m'_p)m'}^b)^* D_{\ell_p(\sigma m_p)m}^b (-1)^{\ell'_p - \sigma m'_p} s_{\sigma m'_p} s_{\sigma m_p} B_{\sigma m'_p - \sigma m_p}^b. \quad (9)$$

The rotation matrices in both forms are defined as appropriate for the two different rotations.

These bond structure factors are of two types, two-center integrals and three-center integrals. The two-center integrals are derived from the terms in Eq. (5) for which $m = 0$, so that $m_p = m'_p$. In this case, $B_0^b = 1$ and $s_{\sigma m_p} s_{\sigma m_p} = 1$ so that the form of the structure factors simplifies considerably, reducing to essentially the form given by Slater and Koster.¹ For these integrals, it is not necessary to compute the symmetry properties of the potential near each bond. All the other terms are called three-center integrals because they involve integrals between orbitals on two sites and a potential centered on a third site. The procedure, outlined above, for finding the structure factors of the three-center matrix elements is the main result of this paper. This procedure has been implemented so that given the location of the atoms and the symmetry operations of the crystal, the independent parameters and their associated structure factors are found automatically.

It is straightforward to determine the independent parameters and their associated structure factors. To find the on-site structure factors for each atom, one first determines the expansion of the potential around each atom, Eq. (2), described in Appendix A. Then, for all possible sets of angular momenta, the structure factor is a simple product, Eq. (3). To determine the bond structure factors, one first tabulates all bonds shorter than a certain length, and then applies all symmetry operations to the bonds to find equivalent bonds, and the sets of operations that take each bond into itself. These sets of operations are used to determine the expansion of the potential around each bond, Eq. (5), as is described in Appendix B. Then the structure factors, Eqs. (6), (8), and (9), are a sum of a small number of terms of rotation matrices for spherical harmonics times the expansion coefficients for the potential. Rotation matrices for spherical harmonics are computed by finding the Euler angles for each rotation.¹⁴

Table I shows the numbers of independent parameters of different types for several simple crystal structures with bonds of various symmetries. The number of two-center parameters is independent of the rotational symmetry of the bond and depends only on whether the two atoms in the bond are equivalent. If the atoms are inequivalent, there are twice as many parameters for $\ell_p \neq \ell'_p$. There are two cases in the table that appear to deviate from this rule; these cases arise when two independent sets of bonds have been grouped together. For the hexagonal close-packed structure, two independent sets of bonds, which have the same length for an ideal hexagonal close-packed structure, have been grouped together in the nearest-neighbor column. For the zincblende structure, the nearest-neighbor bonds within each sublattice have the same length and are grouped together as next-nearest neighbors.

The number of three-center parameters depends on the symmetries of the bonds. Bonds of the same symmetry have the same number of allowed parameters. The next-nearest-neighbor bonds for both the face-centered cubic and the body-centered cubic structures have fourfold symmetry (D_{4h}). The nearest-neighbor bonds for the body-centered cubic and diamond structures are symmetric bonds with threefold symmetry (D_{3d}). Those for the zincblende and wurzite structures are asymmetric bonds with threefold symmetry (C_{3v}).

Since these bonds in the zincblende and wurzite structures are asymmetric, there are twice as many of each kind of parameter. The face-centered cubic nearest neighbors and wurzite next-nearest neighbors have twofold symmetry (D_{2h}) while all other bonds in this table have a simple mirror plane symmetry (C_{2v} with the twofold axes perpendicular to the bonds). Bonds with no symmetry would have still more parameters.

So far in this discussion, the overlap between the orbitals has been ignored. It is possible to do parameterized tight-binding with either orthogonal or non-orthogonal orbitals. Since the underlying orbitals (each typically the product of a spherical harmonic and a radial wave function) are not orthogonal, calculations using orthogonal orbitals invoke Löwdin orthogonalization⁹ to give an orthogonal set of orbitals with the same symmetry properties. In non-orthogonal tight-binding, a form similar to Eq. (1) holds for the overlap matrix, $O_{L,L'}$, parameterized in terms of O_q and O_p . Non-orthogonal fits, first carried out by Mattheiss,⁸ include almost twice as many parameters, allowing much better fits. The overlap matrix depends on all possible parameters except the one-center parameters. If included, the one-center parameters would just effectively rescale all of the other parameters and not otherwise change the fit. If the orbitals were spherical harmonics times radial wave functions, the three-center parameters would be zero for the overlap matrix. However, since the crystal symmetry allows these parameters to be non-zero, including them can increase the quality of the fit.

III. FITTING PROCEDURE

Using Eq. (1) to fit a band structure requires several steps. First, it is necessary to calculate the band structure that is to be fit and to select a subset of these states for fitting. Then, it is necessary to identify the bonds of the crystal structure, their symmetries, and the independent parameters and their associated structure factors. Finally, it is necessary to select fitting criteria, a minimization scheme, and initial values for the parameters.

Selecting states for the fit requires some thought. For example, consider the face-

centered-cubic and body-centered-cubic transition metals which typically have six bands that are below or at the Fermi level. At the zone center, these states have purely s or d character, but, at different parts of the Brillouin zone, the relevant bands have significant p -character. Thus, to obtain a good fit to these band structures it is necessary to include s , p , and d orbitals. For the fit to be meaningful, it is necessary to constrain all of these orbitals. Unfortunately, including the nine lowest states at each wave vector will not work. The problem, which is illustrated in Figs. 1 2, and 3, is that there are bands with f character that cross the bands with p and s character above the Fermi level. The appropriate states can be chosen easily at wave vectors for which the character of the states is restricted by symmetry. At other wave vectors, states must be excluded to avoid introducing unnecessary structure into the bands at high energies. Forcing the fit to reproduce this structure will degrade the fit at all energies. A balance must be found between two requirements. It is necessary to include enough states at high energies to energetically separate the fitting bands from the bands of interest. At the same time, it is important that there not be too much structure in the dispersion of these high energy states that the fit at lower energies is compromised. The appropriate balance must be found by trial and error. Figures 1, 2, and 3 show the results of this balance at energies well above the Fermi level. The bands are kept from the bands of interest, but the fit bands are not very meaningful in this energy range.

The complications described for the simple transition metals are quite general. The orbitals chosen as a basis for the fit must be able to describe the states for which a fit is desired. In general, this will require using more orbitals than there are desired states. Then it is necessary to include additional states in the fit. In most cases these additional states are not separated from states of different symmetry. If they are not, some states of the appropriate symmetry need to be included to keep the the fitting bands from collapsing together, but not so many as to degrade the fit for the bands at lower energy. Because of these complications, fits at energies much above the Fermi level should be considered unreliable unless the fits have been specifically constructed to be accurate in that region.

Determining the symmetries of states is necessary both for deciding which states to

include in the fit, and for insuring that corresponding states are compared in the fit. A state's symmetry is easily determined by computing the character table for each state, a standard group-theoretic technique. This is done for the little group which leaves the state's crystal momentum unchanged. The character table is the "vector" of overlaps between a state and the states that result when each symmetry operation is applied. For degenerate states, it is necessary to compute the vector of the traces of the overlap "matrices," whose rows and columns correspond to symmetry partners. Two states have the same character table if and only if the states have the same symmetry.

Once the bands, for which a fit is desired, have been computed, the appropriate states selected, and the properties of the fitting parameters determined, there are many possible ways to find the fitting parameters. A two-stage minimization procedure that the author has found useful is described below. While this fitting procedure is fairly complicated and is unlikely to be the best possible procedure, it does lead to an adequate fit for all the structures and materials attempted. The procedure is based on the realization that there are many local minima in parameter space, for most of which the resulting fits are poor. Thus, the idea is to first localize the parameters into a part of parameter space that has a low minimum, and then to find that minimum. If the resulting fit is not good enough, the process is repeated until an adequate fit is found.

The first stage of the fitting procedure is broken into several phases. The early phases are designed to align the tight-binding bands with those that are being fit. These phases employ only a few parameters and a small number of wave vectors. Subsequent phases introduce more parameters and more wave vectors. Throughout the first stage a simplex minimization algorithm¹¹ is used. This algorithm is good at exploring phase space, particularly when used in combination with simulated annealing.¹¹ It also provides a straightforward way to add parameters during the minimization. The simplex algorithm is based on a set of rules that are applied to a set, called a simplex, of sets of possible values of the fitting parameters. If there are N parameters, there are $N + 1$ sets in the simplex. When parameters are added to the minimization, the size of the simplex is increased. The new simplex is taken to be the old

simplex with the values of all new parameters set to zero, plus a new set of parameters for each of parameters that is being added. The new sets are the set from the original simplex with the lowest value of the fitting function with random values for the new parameters. In this way, none of the old information about the minimization is lost, but the algorithm rapidly finds values of the new parameters that improve the fit.

In more detail, one first assigns random values to the on-site, crystal-field, and nearest-neighbor two-center Hamiltonian parameters. A preliminary fit at a few wave vectors is obtained by use of simulated annealing. During this first stage of fitting, the bands at high-symmetry points are weighted higher than those at low-symmetry points. This is done because at high-symmetry points it is easier to ensure that the proper bands are coupled together in the minimization function. Eventually, the “temperature” of the simulated annealing reaches zero, where it is kept for the rest of the fitting procedure. In the next phases more wave vectors are added to the fit while more and more parameters are included. When new parameters are included they are started with random values. First one adds the next-nearest-neighbor Hamiltonian parameters, then the overlap parameters, and finally the three-center parameters.

The disadvantage of the simplex algorithm for minimization is that it is quite slow to converge to the minimum. The simplex algorithm is used only to get the parameters into a valley of phase space that (hopefully) has a low minimum. Then, in the second stage, two minimizations are computed with a much faster modified Levenberg-Marquardt¹³ algorithm. The first uses larger weightings for the high-symmetry points and the second uses the weightings as appropriate for a special k-points method of Brillouin zone integration.¹² The first of these is done to make sure the correct bands remain coupled with each other in the minimization. The second polishes the values of the parameters to make the fit more uniform over the whole Brillouin zone. Testing the quality of the fit after this last minimization determines whether the fit needs to be repeated with a different set of random initial values.

Figures 1, 2, and 3 show band structures for face-centered cubic, body-centered cubic, and

hexagonal close-packed structures respectively, both from calculations done with a linearized-augmented-plane-wave (LAPW) method and from the corresponding non-orthogonal tight-binding fits. For the bands that cross the Fermi level, the root-mean-square deviations comparing the fit bands and the LAPW bands are 8 meV, 5 meV, and 2 meV respectively, for the three different structures. Across the transition metal series for face-centered cubic and body-centered cubic structures, I have found fits¹⁰ that on average are better, but not significantly, than those found by Papaconstantopoulos.⁷ For the hexagonal close-packed structures, Papaconstantopoulos did not compute three-center fits, and the present fits are better by more than an order of magnitude than the two-center fits he reported. For a few materials, several fits were found of comparable accuracy but with completely different fitting parameters. The existence of several local minima of comparable depth indicates the non-uniqueness of seemingly very good fits.

IV. SUMMARY

I have presented a procedure for fitting band structures of materials with arbitrary crystal structures. It is a generalization of the Slater-Koster two-center approximation that includes all independent three-center contributions. Including the three-center contributions increases the number of independent parameters. The increased number of parameters allows more accurate fits to be made. This procedure was demonstrated by fitting the bands for face-centered cubic, body-centered cubic, and hexagonal close-packed transition metals.

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APPENDIX A: ON-SITE STRUCTURE FACTORS

The form of the tight-binding matrices to be used for the parameterizations is most easily found by considering the matrix elements of the periodic potential. The on-site matrix elements are simplified by writing the potential around each atom as a sum over

all symmetry allowed terms as in Eq. (2). When symmetry operations of the crystal that map an atom into itself, \widehat{M}^i , are applied to the potential around that atom, they change spherical harmonics into other spherical harmonics with the same angular momentum, ℓ ,

$$\widehat{M}^i \left[\sum_{\nu} V^{\nu}(r) \sum_{m=-\ell_{\nu}}^{\ell_{\nu}} C_{j,m}^{\nu} Y_{\ell_{\nu}m}(\hat{\mathbf{r}}) \right] = \sum_{\nu} V^{\nu}(r) \sum_{m'=-\ell_{\nu}}^{\ell_{\nu}} \left[\sum_{m=-\ell_{\nu}}^{\ell_{\nu}} C_{j,m}^{\nu} M_{m,m'}^{i\ell} \right] Y_{\ell m'}(\hat{\mathbf{r}}). \quad (\text{A1})$$

The combinations of spherical harmonics, C_{jm}^s , in Eq. (2) that are consistent with the symmetry of the crystal must be eigenvectors of each of the symmetry matrices, $M_{m,m'}^{i\ell}$, with an eigenvalue for each operation equal to one. These combinations can be found by summing the matrices $M^{i\ell}$ over all operations, i , that map the atom into itself

$$M_{m,m'}^{\ell} = \sum_i M_{m,m'}^{i\ell}. \quad (\text{A2})$$

For high symmetry atoms and low angular momenta, most, if not all, of the eigenvalues of the resulting matrix are zero. The allowed combinations are just the eigenvectors of M^{ℓ} with non-zero eigenvalues.

If some symmetry operations map the atom into different atoms in the unit cell, the symmetry factors for those atomic sites are related. Once they have been found for one atom, they can be found for related atoms using the operation that relates them. In this case, the parameters for these related atoms are not independent.

Substituting in the form of the potential in Eq. (2) into the on-site matrix element gives

$$V_{L,L'}^{\text{on-site}}(\mathbf{k}) = \delta_{j,j'} \sum_{\nu} \sum_{j'' \in \{j_{\nu}\}} \delta_{j,j''} \sum_{m''=-\ell_{\nu}}^{\ell_{\nu}} C_{jm''}^{\nu} G(\ell m, \ell_{\nu} m'', \ell' m') V_{\nu \ell \ell'}, \quad (\text{A3})$$

where G is a Gaunt coefficient, and $V_{\nu \ell \ell'}$ is the radial integral of the potential and the two radial wave functions

$$V_{\nu \ell \ell'} = \int_0^{\infty} dr r^2 \phi_{j\ell}(r) V^{\nu}(r) \phi_{j'\ell'}(r). \quad (\text{A4})$$

These radial matrix elements will become on-site fitting parameters H^q when an equivalent contribution from the kinetic energy is added.

APPENDIX B: BOND STRUCTURE FACTORS

When calculating the contribution to the potential matrix elements from the bonds, it is useful to rotate each bond into the z -direction (or negative z -direction) to take advantage of the form of the spherical harmonics. The angles are rotated about an axis perpendicular to both $\hat{\mathbf{z}}$ and $\hat{\mathbf{R}}_b$; the rotation of the spherical harmonics is given by

$$Y_{\ell m}(\hat{\mathbf{r}}) = \sum_{m'=-\ell}^{\ell} D_{\ell m' m}^b Y_{\ell m'}(\mathbf{R}^{-1}\hat{\mathbf{r}}), \quad (\text{B1})$$

where $\mathbf{R}^{-1}\hat{\mathbf{r}}$ are the rotated coordinates that are aligned with the bond. Substituting the rotated spherical harmonics in to the bond matrix elements and replacing the full Hamiltonian by the potential gives

$$V_{L,L'}^{\text{bond}}(\mathbf{k}) = \sum_b \delta_{j,j_{1b}} \delta_{j',j_{0b}} e^{i\mathbf{k}\cdot\mathbf{R}_b} \sum_{m''=-\ell}^{\ell} \sum_{m'''=-\ell'}^{\ell'} (D_{\ell m'' m}^b)^* D_{\ell' m''' m'}^b \int d^3r Y_{\ell m''}(\mathbf{R}^{-1}\hat{\mathbf{r}}_b)^* \phi_{j\ell}(r_b) V(\mathbf{r} + \mathbf{r}_{j'}) Y_{\ell' m'''}(\mathbf{R}^{-1}\hat{\mathbf{r}}) \phi_{j'\ell'}(r). \quad (\text{B2})$$

Since the spherical harmonics are defined around different centers, the azimuthal integration around the bond axis has useful orthogonality properties, but the others do not. For this reason it is useful to write the spherical harmonics as

$$Y_{\ell m}(\mathbf{R}^{-1}\hat{\mathbf{r}}) = A_{\ell m} s_m P_{\ell m}(\cos \theta) e^{im\phi}, \quad (\text{B3})$$

where $A_{\ell m}$ is a positive real normalization constant, and s_m is a sign that enters from the definition of spherical harmonics in terms of associated Legendre polynomials defined in Eq. (7). The integral in Eq. (B2) over ϕ is done analytically, and the others are parameterized.

To carry out these integrals it is useful to rewrite the potential around the bond in cylindrical coordinates: the azimuthal angle, ϕ , defined above the distance along the bond, z , and the radial distance from the bond, ρ . In these coordinates, the potential along the bond can be written as in Eq. (5). The bond symmetry factors, B_m^b , may be zero or a phase as determined by the symmetry around the bond. Since the potential is real, $B_{-m}^b = (B_m^b)^*$. Symmetry operations of the crystal that map the bond into itself, $\widehat{\mathbf{M}}^i$, change exponential

factors $e^{\pm im\phi}$ into linear combinations of the same exponential factors without changing the function of the other coordinates:

$$\widehat{M}^i \left[\sum_m V_{b,|m|}(\rho, z) B_m^b e^{im\phi} \right] = \sum_{m'} V_{b,|m'|}(\rho, z) \left[\sum_{m=\pm m'} B_m^b M_{m,m'}^i \right] e^{im'\phi}. \quad (\text{B4})$$

The combinations of exponential factors that are consistent with the symmetry of the crystal must be eigenvectors of each of the symmetry matrices, $M_{m,m'}^i$, with the same eigenvalue for each operation. The eigenvectors are determined by summing the matrices M^i over all operations that leave the bond invariant

$$M_{m,m'} = \sum_i M_{m,m'}^i. \quad (\text{B5})$$

If the matrix, M^m is zero for a given azimuthal quantum number, then no combination is consistent, as is the case for high symmetry bonds. If there is one non-zero eigenvalue of the matrix, then there is one linear combination of $e^{im\phi}$ and $e^{-im\phi}$ that is consistent with the symmetry, and the eigenvector of M^m gives the allowed combination. If there are two non-zero eigenvalues, they will be the same and there are two factors, B_m^b and $B_m'^b$, that must be included. This case only occurs if the identity operation is the only operation that takes the bond into itself. I will ignore this case in rest of this derivation.

Since the eigenvector is only defined up to an arbitrary factor, it is necessary to ensure that the symmetry factors for equivalent bonds are defined equivalently. This complication can be addressed by choosing one bond from a set of equivalent bonds and finding the symmetry factors for it. The prescription in Eq. (B1) for rotating the bonds into the z -direction leaves each bond rotated around the z -direction with respect to this chosen bond. Using this rotation, it is straightforward to find the symmetry factors for each bond from that for the chosen bond.

Starting from Eq. (B2), rotating the spherical harmonics as in Eq. (B3), substituting Eq. (5) for the potential, carrying out the integrations, and summing over Kronecker delta functions gives

$$V_{L,L'}^{\text{bond}}(\mathbf{k}) = \sum_b \delta_{j,j_{1b}} \delta_{j',j_{0b}} e^{i\mathbf{k} \cdot \mathbf{R}_b}$$

$$\sum_{m''=-\ell}^{\ell} \sum_{m'''=-\ell'}^{\ell'} (D_{\ell m'' m}^b)^* D_{\ell' m''' m'}^b (-1)^{\ell-m''} s_{m''} s_{m'''} B_{m''-m'''}^b V_{b,\ell,\ell',m'',m'''}, \quad (\text{B6})$$

where

$$V_{b,\ell,\ell',m'',m'''} = \int_{-\infty}^{\infty} dz \int_0^{\infty} \rho d\rho (-1)^{\ell-m''} P_{\ell m''}(\cos \theta_b) \phi_{j\ell}(r_b) V_{b,m''-m'''}(\rho, z) P_{\ell' m'''}(\cos \theta) \phi_{j'\ell'}(r). \quad (\text{B7})$$

Here θ and r are defined relative to the end of the bond at the j' atomic site and θ_b and r_b are defined relative to the other end of the bond at \mathbf{R}_b . These arguments are functions of the variables ρ and z . The factor, $(-1)^{\ell-m''}$, insures that the lobe of the spherical harmonic pointing toward the center of the bond is positive for both of the polynomials in the integrand. The parameters $V_{b,\ell,\ell',m'',m'''}$ will be fitting parameters, but they need to be grouped together so that all that are related by symmetry are not treated as independent parameters. Each independent parameter is defined for a set of equivalent bonds, $\{b_p\}$.

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FIGURES

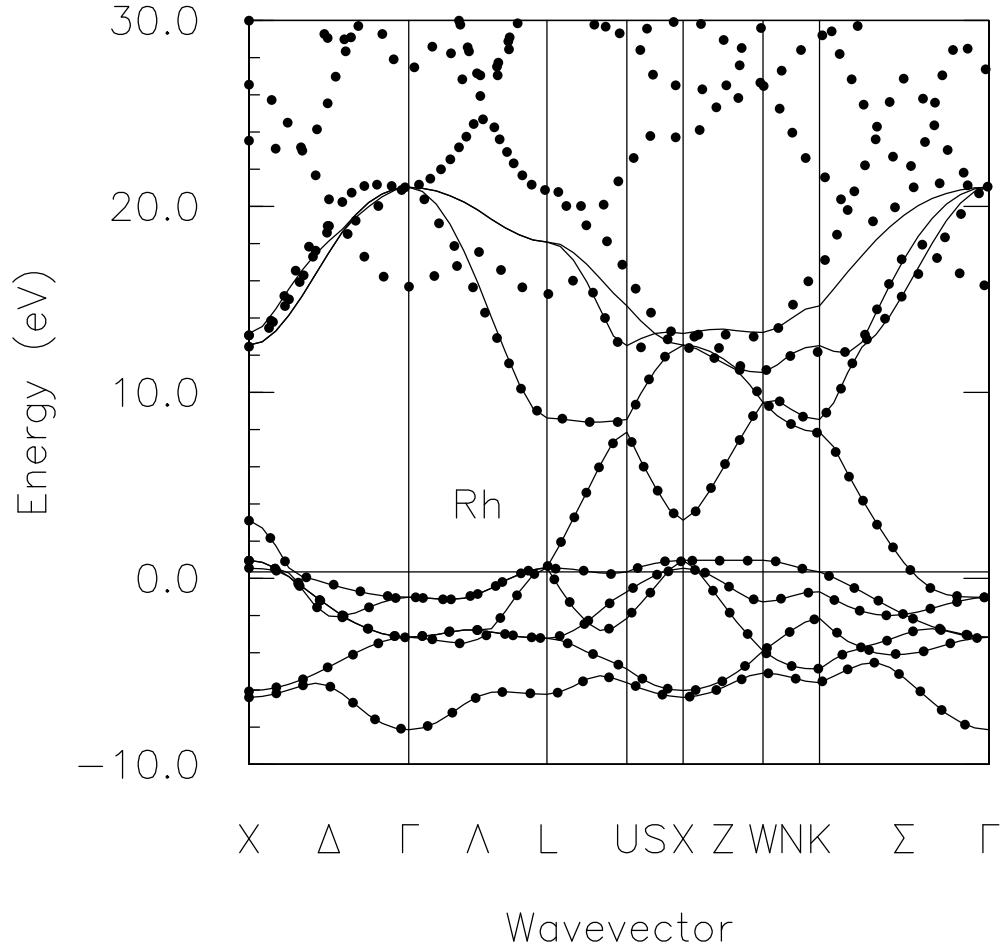


FIG. 1. Band structure for face-centered cubic Rh. The filled circles are the band structure calculated with the LAPW program in the LDA. The lines are the tight-binding fits to these bands.

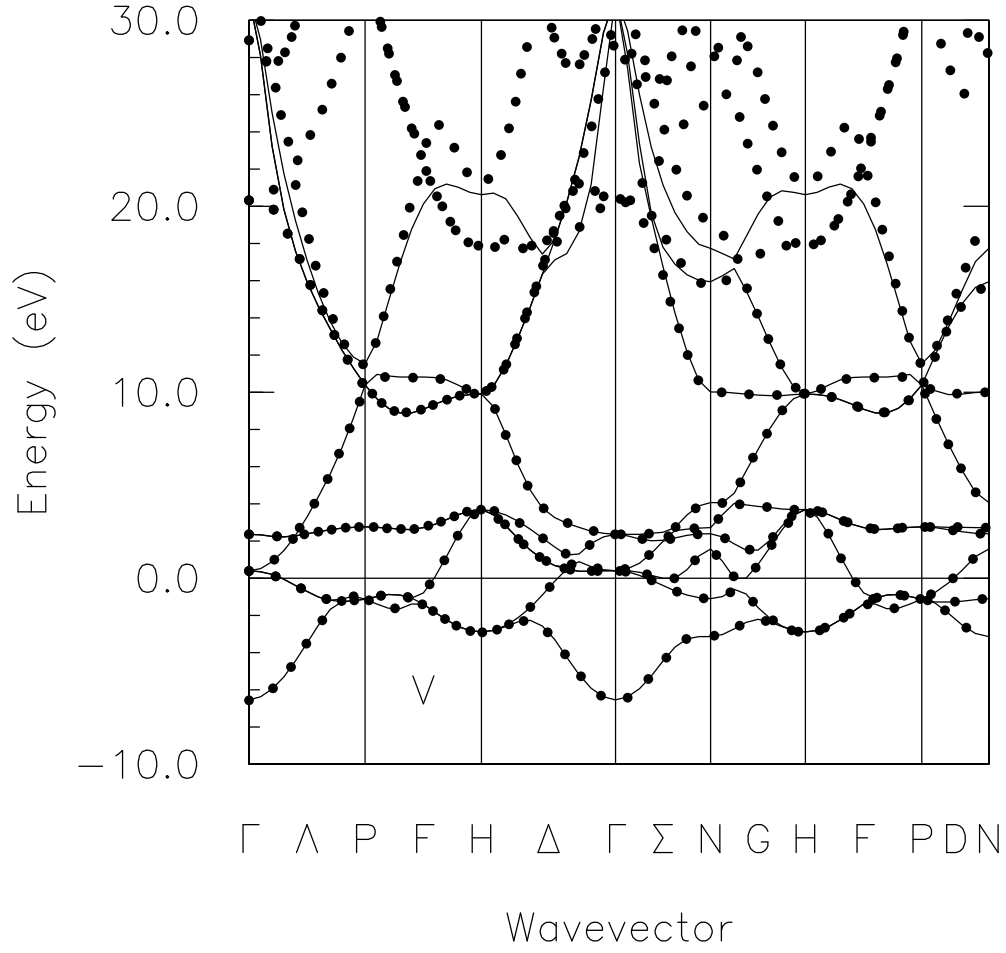


FIG. 2. Band structure for body-centered cubic V. The filled circles are the band structure calculated with the LAPW program in the LDA. The lines are the tight-binding fits to these bands.

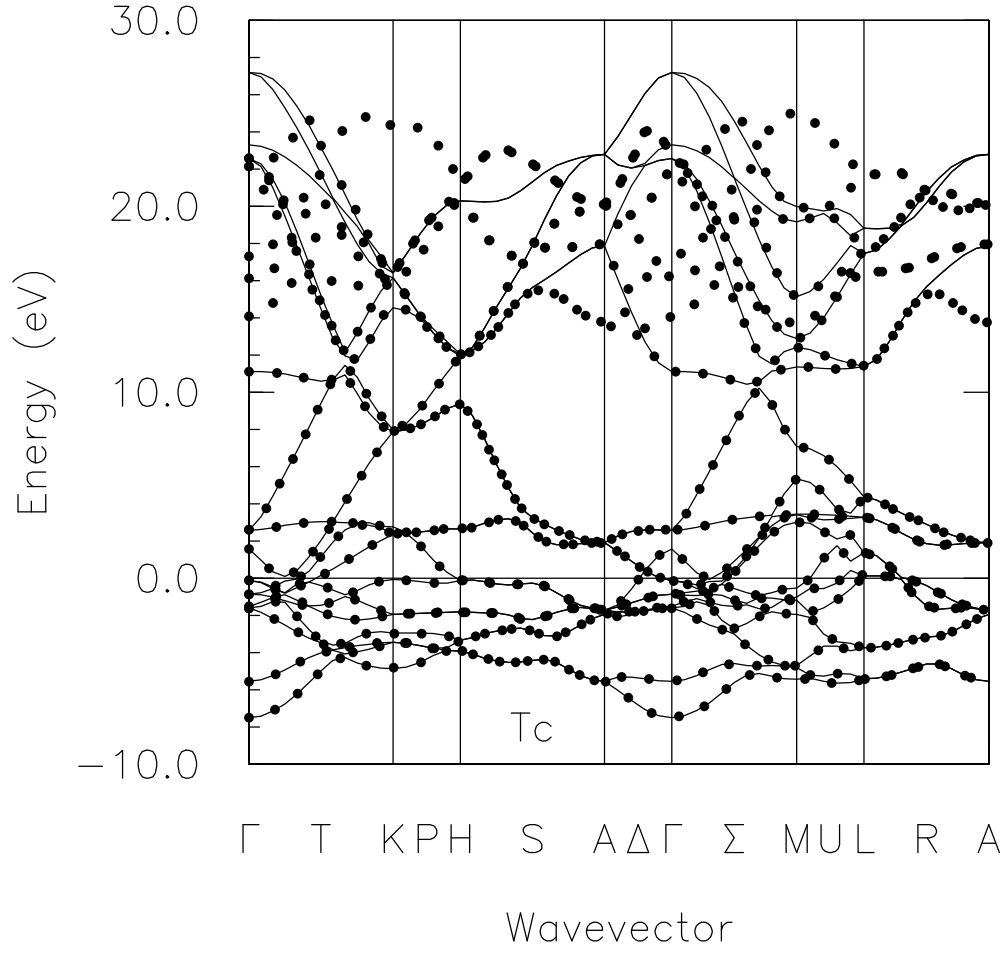


FIG. 3. Band structure for hexagonal close-packed Tc. The filled circles are the band structure calculated with the LAPW program in the LDA. The lines are the tight-binding fits to these bands.

TABLES

TABLE I. Numbers of parameters of different types for different crystal structures. The table gives the number of one-center O_1 , crystal-field, O_{CF} , two-center, NN_2 , and three-center, NN_3 , for nearest-neighbor bonds and two-center, NNN_2 , and three-center, NNN_3 , for next-nearest-neighbor bonds, For the hexagonal close-packed structure, the two shortest neighbor bonds have been grouped together. In an ideal hexagonal close-packed structure these two sets of bonds would have the same length. For the zincblende and wurzite structures there are two inequivalent atoms, so the number of on-site terms is increased correspondingly.

	O_1	O_{CF}	NN_2	NN_3	NNN_2	NNN_3
face-centered cubic						
$s-s$	1	0	1	0	1	0
$s-p$	0	0	1	0	1	0
$p-p$	1	0	2	1	2	0
$s-d$	0	0	1	1	1	0
$p-d$	0	0	2	2	2	0
$d-d$	1	1	3	3	3	1
body-centered cubic						
$s-s$	1	0	1	0	1	0
$s-p$	0	0	1	0	1	0
$p-p$	1	0	2	0	2	0
$s-d$	0	0	1	0	1	0
$p-d$	0	0	2	1	2	0
$d-d$	1	1	3	1	3	1
hexagonal close-packed						
$s-s$	1	0	2	0	1	0
$s-p$	0	0	2	2	1	1
$p-p$	1	1	4	4	2	2

<i>s-d</i>	0	1	4	4	1	2
<i>p-d</i>	0	1	4	10	2	5
<i>d-d</i>	1	2	6	12	3	6
diamond						
<i>s-s</i>	1	0	1	0	1	0
<i>s-p</i>	0	0	1	0	1	1
<i>p-p</i>	1	0	2	0	2	2
<i>s-d</i>	0	0	1	0	1	2
<i>p-d</i>	0	1	2	1	2	5
<i>d-d</i>	1	1	3	1	3	6
zinblend						
<i>s-s</i>	2	0	1	0	2	0
<i>s-p</i>	0	0	2	0	2	2
<i>p-p</i>	2	0	2	0	4	4
<i>s-d</i>	0	0	2	0	2	4
<i>p-d</i>	0	2	4	2	4	10
<i>d-d</i>	2	2	3	2	6	12
wurzite						
<i>s-s</i>	2	0	1	0	1	0
<i>s-p</i>	0	0	2	0	1	0
<i>p-p</i>	2	0	2	0	2	1
<i>s-d</i>	0	0	2	0	1	1
<i>p-d</i>	0	1	4	2	2	2
<i>d-d</i>	2	2	3	2	3	3
