

Applications of the quadratic Korringa-Kohn-Rostoker band-theory method

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Comparisons with other calculations in the literature are used to demonstrate that the quadratic Korringa-Kohn-Rostoker band-theory method gives excellent eigenvalues for full self-consistent potentials with no shape approximation. The equations for the Green function are reformulated, thus eliminating a problem that had hampered calculations of self-consistent potentials and total energies with the use of this method.

I. INTRODUCTION

The Korringa-Kohn-Rostoker^{1,2} (KKR) method differs from other band-theory methods in that it is derived from the multiple-scattering theory.³ It has the great advantage that it does not require explicit orthogonalization to core states, the orthogonality of the conduction-band wave functions to the core functions arising from the formalism. The eigenvalues are the roots of a secular determinant which is quite small compared to the ones that occur in other theories, but all of the matrix elements depend on energy in a complicated way. The multiple-scattering theory has been used to derive another method⁴ called the quadratic KKR (QKKR), which retains the advantages of the KKR and circumvents some of its drawbacks. The derivation is based on equations derived in Ref. 5. A major advantage of the QKKR is that all of the eigenvalues for a given \mathbf{k} are obtained from one matrix diagonalization. There are a number of band-theory techniques based on the Rayleigh-Ritz variational method that share this advantage. They include such methods as linear augmented-plane-wave⁶ (LAPW), linear combination of Gaussian orbitals⁷ (LCGO), linear muffin-tin orbitals⁸ (LMTO) and linear augmented-spherical-wave (LASW) methods.⁹ These methods either require the diagonalization of a much larger matrix than the QKKR or they yield accurate eigenvalues over a smaller range of energies.

Another advantage of the QKKR is that it does not require any shape approximation in the self-consistent (SC) potential function. As it was originally derived, the KKR theory appeared to require that the SC potential must have the muffin-tin form. Self-consistent muffin-tin (SCMT) potentials are spherically symmetric within spheres, constant outside, and the spheres cannot overlap. Full SC potentials for metals can be approximated by SCMT potentials with no great loss of accuracy, but this is not true for covalent or ionic materials. Even for metals, the muffin-tin approximation can lead to difficulties in precise calculations of the total energy. It will be obvious from the equations in this paper that it is no more difficult to carry out a QKKR calculation with a

full SC than a SCMT potential. Computational results are shown that demonstrate the applicability of the QKKR theory to potentials with no shape approximation.

The price that must be paid for its advantages is that the algebra of the QKKR seems somewhat more convoluted than that used in the other methods, particularly to those who are not very familiar with the multiple-scattering theory¹⁻³ of Rayleigh, Kasterin, Ewald, Korringa, Lax, and Kohn. The development of a self-consistent version of the QKKR as well as programs for calculating the total energy was, in fact, slowed by a subtlety in the algebra that was not understood until recently. The problem was difficult to recognize because it appears only in the evaluation of the Green function, not the eigenvalues, and the errors it causes are so small that they were thought to be due to a lack of convergence. Now that a cure has been found,¹⁰ all aspects of the calculations are behaving correctly, as will be demonstrated.

An equation for the Green function is derived in the next section within the QKKR formalism, and the difficulty that arises in its evaluation is pointed out. A reformulation of the equation that eliminates that difficulty is given in the following section. Numerical examples of the application of the QKKR are presented in Sec. IV. In the last section, the future developments that can be expected from this theory are discussed.

II. GREEN FUNCTION FOR THE PERFECT CRYSTAL

The mathematics of the QKKR band-theory technique starts with a simple observation⁵ about the one-electron Schrödinger equation

$$[-\nabla^2 + V(\mathbf{r})]\psi_{\mathbf{k}}^{\alpha}(\mathbf{r}) = E_{\alpha}(\mathbf{k})\psi_{\mathbf{k}}^{\alpha}(\mathbf{r}). \quad (1)$$

The potential $V(\mathbf{r})$ that is obtained from the local-density approximation may be written as a sum of potentials

$$V(\mathbf{r}) = \sum_n v(\mathbf{r} - \mathbf{R}_n) \quad (2)$$

by partitioning it so that $v(\mathbf{r})$ is zero outside the unit cell. Subtracting the same constant from the eigenvalue and the potential, (1) is transformed into

$$[-\nabla^2 + V^\Delta(\mathbf{r})]\psi_{\mathbf{k}}^\Delta(\mathbf{r}) = E_0\psi_{\mathbf{k}}^\Delta(\mathbf{r}), \quad (3)$$

where the potential $V^\Delta(\mathbf{r})$ is a sum of potentials

$$v^\Delta(\mathbf{r}) = v(\mathbf{r}) - \Delta\sigma(\mathbf{r}). \quad (4)$$

The value of the unit step function $\sigma(\mathbf{r})$ is 1 when \mathbf{r} is inside the unit cell, and 0 elsewhere. It is clear that

$$\psi_{\mathbf{k}}^\Delta(\mathbf{r}) = \psi_{\mathbf{k}}^\alpha(\mathbf{r}) \quad (5)$$

when the constant Δ is equal to

$$\Delta_\alpha(\mathbf{k}) = E_\alpha(\mathbf{k}) - E_0. \quad (6)$$

Thus band-theory calculations can be carried out in a mode in which the wave functions all correspond to the same eigenvalue, but the potential is continuously shifted. The advantages of this approach will be described.

The eigenfunctions can be expanded as the linear combination

$$\psi_{\mathbf{k}}^\Delta(\mathbf{r}) = \sum_L \phi_L^\Delta(\mathbf{r}) d_L^\Delta(\mathbf{k}), \quad (7)$$

where the $\phi_L^\Delta(\mathbf{r})$ are solutions of

$$[-\nabla^2 + v^\Delta(\mathbf{r})]\phi_L^\Delta(\mathbf{r}) = E_0\phi_L^\Delta(\mathbf{r}) \quad (8)$$

that satisfy the boundary condition

$$\lim_{r \rightarrow 0} \phi_L^\Delta(\mathbf{r}) = Y_L(\mathbf{r}) j_l(\kappa_0 r), \quad (9)$$

and are continuous. The constant κ_0 is the square root of E_0 , $j_l(x)$ is a spherical Bessel function, $Y_L(\mathbf{r})$ is a real spherical harmonic, and $L = \{l, m\}$ is a collective angular momentum index. It has been shown⁵ that $\phi_L^\Delta(\mathbf{r})$ can be obtained by iteration from the integral equation

$$\phi_L^\Delta(\mathbf{r}) = Y_L(\mathbf{r}) j_l(\kappa_0 r) + \int_{r' < r} K(\mathbf{r}, \mathbf{r}') v^\Delta(\mathbf{r}') \phi_L^\Delta(\mathbf{r}') d\mathbf{r}', \quad (10)$$

where the kernel is

$$K(\mathbf{r}, \mathbf{r}') = -\kappa_0 \sum_L Y_L(\mathbf{r}) [j_l(\kappa_0 r) n_l(\kappa_0 r') - n_l(\kappa_0 r) j_l(\kappa_0 r')] Y_L(\mathbf{r}'). \quad (11)$$

For $r > 0$, $\phi_L^\Delta(\mathbf{r})$ can be expanded in spherical harmonics

$$\phi_L^\Delta(\mathbf{r}) = \sum_{L'} Y_{L'}(\mathbf{r}) \phi_{L'L}^\Delta(r). \quad (12)$$

It follows from the KKR theory for SC potentials that have no special shape⁵ that the coefficients $d_L^\Delta(\mathbf{k})$ in (7) are solutions of the set of homogeneous algebraic equations

$$\sum_{L'} D_{LL'}^\Delta(\mathbf{k}) d_L^\Delta(\mathbf{k}) = 0, \quad (13)$$

where the matrix $D^\Delta(\mathbf{k})$ is

$$D^\Delta(\mathbf{k}) = \kappa_0 \underline{C}^\Delta + \underline{B}(E_0, \mathbf{k}) \underline{S}^\Delta. \quad (14)$$

The elements of $\underline{B}(E_0, \mathbf{k})$ are taken to be the ordinary structure constants of KKR theory that were derived for the special case of muffin-tin potentials.^{1,2} There has been a hot debate in the recent literature¹¹ concerning the existence of near-field corrections (NFC) that should be added to these structure constants when potentials that are not of the muffin-tin form are used. The outcome of this debate is that the NFC are either negligible or nonexistent for all cases studied so far.

The cosine and sine matrices, \underline{C}^Δ and \underline{S}^Δ , are obtained⁵ from the equations

$$\underline{C}_{LL'}^\Delta = \kappa_0 \int n_l(\kappa_0 r) Y_L(\mathbf{r}) v^\Delta(\mathbf{r}) \phi_{L'}^\Delta(\mathbf{r}) d\mathbf{r} - \delta_{LL'}, \quad (15)$$

$$\underline{S}_{LL'}^\Delta = \kappa_0 \int j_l(\kappa_0 r) Y_L(\mathbf{r}) v^\Delta(\mathbf{r}) \phi_{L'}^\Delta(\mathbf{r}) d\mathbf{r}.$$

The t matrix that describes the scattering of an incoming wave of energy E_0 from the isolated potential $v^\Delta(\mathbf{r})$ is such that

$$[\underline{T}^\Delta(E_0)]^{-1} = \kappa_0 \underline{C}^\Delta (\underline{S}^\Delta)^{-1} + i\kappa_0. \quad (16)$$

The matrix elements of \underline{C}^Δ and \underline{S}^Δ are entire functions of Δ , which means that the matrices may be written as Taylor's series

$$\underline{C}^\Delta = \underline{C}^{(0)} + \underline{C}^{(1)}\Delta + \underline{C}^{(2)}\Delta^2 + \dots, \quad (17)$$

$$\underline{S}^\Delta = \underline{S}^{(0)} + \underline{S}^{(1)}\Delta + \underline{S}^{(2)}\Delta^2 + \dots.$$

The eigenvalues $\Delta_\alpha(\mathbf{k})$ in (6) are, from (13), the values of Δ for which

$$\det \underline{D}^\Delta(\mathbf{k}) = 0. \quad (18)$$

Calculating these eigenvalues for a given \mathbf{k} requires that Eqs. (10) and (15) must be solved and the determinant in (18) evaluated for very many values of Δ . Such a calculation is essentially exact, but it is even more time consuming than one done with the ordinary KKR method. However, these equations provide the basis for some very useful approximations. Inserting the Taylor's expansion of (17) into (14) leads to

$$\underline{D}^\Delta(\mathbf{k}) = \underline{H} - \underline{Q}\Delta + \underline{A}\Delta^2 + \dots, \quad (19)$$

with

$$\begin{aligned} \underline{H}(\mathbf{k}) &= \kappa_0 \underline{C}^{(0)} + \underline{B}(E_0, \mathbf{k}) \underline{S}^{(0)}, \\ \underline{Q}(\mathbf{k}) &= -\kappa_0 \underline{C}^{(1)} - \underline{B}(E_0, \mathbf{k}) \underline{S}^{(1)}, \\ \underline{A}(\mathbf{k}) &= \kappa_0 \underline{C}^{(2)} + \underline{B}(E_0, \mathbf{k}) \underline{S}^{(2)}. \end{aligned} \quad (20)$$

Ignoring the matrix $\underline{A}(\mathbf{k})$ and all coefficients of higher powers of Δ would lead to a linearized version of the KKR (LKRR). Approximations to the eigenvalues $\Delta_\alpha(\mathbf{k})$ are found from a single diagonalization of a matrix $\underline{E}(\mathbf{k})$,

$$\underline{E}(\mathbf{k}) = \underline{Q}^{-1}(\mathbf{k}) \underline{H}(\mathbf{k}). \quad (21)$$

All of these matrices are made finite in the usual way, by ignoring elements corresponding to values of angular momentum greater than some l_{\max} . The dimension of these matrices is then $(l_{\max} + 1)^2$. An algebraic comparison between this LKRR and other linearized band

theories that are related to the KRR, the LMTO and the LASW, was given in an earlier paper.⁵ The LKKR eigenvalues for a niobium potential are compared with the exact eigenvalues in Fig. 5 of Ref. 4, and can be seen to be disappointing if very accurate eigenvalues are desired over the entire range of the conduction band.

The quadratic KKR (QKKR) is obtained⁴ by including the next term in the expansion in (19). The eigenvalues for a given \mathbf{k} are again found by diagonalizing a single matrix which has a dimension that is twice that of $\underline{E}(\mathbf{k})$, $2(l_{\max} + 1)^2$. The value of l_{\max} that has proven most satisfactory in the calculations done to date is four, so this dimension is 50. The QKKR eigenvalues for niobium can be seen from Fig. 5 or Ref. 4 to agree very well with the exact ones. At this point we are more interested in the Green function since that is the quantity that is needed in self-consistent calculations and in the evaluation of total energies.

By a straightforward transformation of a previous result¹² it can be shown that the Green function for a periodic solid can be written

$$G^{\Delta}(\mathbf{r}, \mathbf{r}') = \frac{1}{\Omega} \int G_{\mathbf{k}}^{\Delta}(\mathbf{r}, \mathbf{r}') d\mathbf{k}, \quad (22)$$

where Ω is the volume of the Brillouin zone, with

$$G_{\mathbf{k}}^{\Delta}(\mathbf{r}, \mathbf{r}') = \sum_{L, L'} Z_L^{\Delta}(\mathbf{r}) \tau_{LL'}^{\Delta}(\mathbf{k}) Z_{L'}^{\Delta}(\mathbf{r}') - \sum_L Z_L^{\Delta}(\mathbf{r}) J_L^{\Delta}(\mathbf{r}'). \quad (23)$$

The function $Z_L^{\Delta}(\mathbf{r})$ is defined by

$$Z_L^{\Delta}(\mathbf{r}) = \kappa_0 \sum_{L'} \phi_{L'}^{\Delta}(\mathbf{r}) [(\underline{S}^{\Delta})^{-1}]_{L'L} \quad (24)$$

and the matrix τ^{Δ} is the inverse of the symmetrical KKR matrix. We write

$$\underline{M}^{\Delta} = -\kappa_0 \underline{C}^{\Delta} (\underline{S}^{\Delta})^{-1} - \underline{B}(E_0, \mathbf{k}). \quad (25)$$

The function $J_L^{\Delta}(\mathbf{r})$ is the solution of (8) that satisfies the boundary condition

$$\lim_{r \rightarrow \infty} J_L^{\Delta}(\mathbf{r}) = Y_L(\mathbf{r}) j_l(\kappa_0 r). \quad (26)$$

For most values of Δ this function approaches infinity as r approaches zero.

The Green function can be rewritten

$$G_{\mathbf{k}}^{\Delta}(\mathbf{r}, \mathbf{r}') = \kappa_0 \sum_L \phi_L^{\Delta}(\mathbf{r}) W_L^{\Delta}(\mathbf{r}'), \quad (27)$$

with

$$W_L^{\Delta}(\mathbf{r}) = -\kappa_0 \sum_{L', L''} F_{LL'}^{\Delta} [(\underline{S}^{\Delta})^{-1}]_{L'L''} \phi_{L''}^{\Delta}(\mathbf{r}) - \sum_{L'} [(\underline{S}^{\Delta})^{-1}]_{LL'} J_{L'}^{\Delta}(\mathbf{r}). \quad (28)$$

The matrix \underline{F}^{Δ} is the inverse of the \underline{D}^{Δ} defined in (14), and it follows that it can be expanded in terms of the eigenvalues of \underline{D}^{Δ}

$$\underline{F}^{\Delta}(\mathbf{k}) = \sum_{\alpha} \frac{\underline{F}^{\alpha}(\mathbf{k})}{\Delta - \Delta_{\alpha}(\mathbf{k})}. \quad (29)$$

In the QKKR the dimension of $\underline{F}^{\alpha}(\mathbf{k})$ is $2(l_{\max} + 1)^2$, and there are that many terms in the sum. The valence charge density is calculated by an integration over the Brillouin zone,

$$\rho(\mathbf{r}) = \frac{1}{\Omega} \int A(\mathbf{k}, \mathbf{r}, \mathbf{r}') d\mathbf{k}, \quad (30)$$

where the function $A(\mathbf{k}, \mathbf{r}, \mathbf{r}')$ is obtained by integrating the Green's function from the bottom of the band Δ_b to the Fermi energy $\Delta_F = E_F - E_0$:

$$A(\mathbf{k}, \mathbf{r}, \mathbf{r}') = -\frac{1}{\pi} \text{Im} \int_{\Delta_b}^{\Delta_F} G_{\mathbf{k}}^{\Delta}(\mathbf{r}, \mathbf{r}') d\Delta. \quad (31)$$

This integration can be carried out along any trajectory. If it is carried out along the real axis, all of the functions and matrices in $G_{\mathbf{k}}^{\Delta}(\mathbf{r}, \mathbf{r}')$ are real, so the only imaginary parts in the integrand arise from the poles in the sum in (29). This will lead to an expression for $A(\mathbf{k}, \mathbf{r}, \mathbf{r}')$ that is a sum of wave functions evaluated at the eigenvalues $\Delta_{\alpha}(\mathbf{k})$, as might be expected.

The fact that the determinant of the sine matrix \underline{S}^{Δ} is zero for a set of energies Δ_n^s must be taken into account. It follows that the inverse of the sine matrix can be expanded as a sum

$$(\underline{S}^{\Delta})^{-1} = \sum_n \frac{\underline{S}^n}{\Delta - \Delta_n^s}, \quad (32)$$

and there should be contributions to the imaginary part of $G_{\mathbf{k}}^{\Delta}(\mathbf{r}, \mathbf{r}')$ from both inverses in (28). A very careful analysis shows that these two contributions cancel each other, so that the function $J_L^{\Delta}(\mathbf{r})$ does not appear in the imaginary part of the Green function. The charge density can be found by integrating over \mathbf{k} the contributions

$$A(\mathbf{k}, \mathbf{r}, \mathbf{r}') = -E_0 \sum_{\substack{\alpha, n \\ L, L'}} \phi_L^{\Delta}(\mathbf{r}) \frac{Q_{LL'}^{\alpha n}}{\Delta_{\alpha}(\mathbf{k}) - \Delta_n^s} \phi_{L'}^{\Delta}(\mathbf{r}'). \quad (33)$$

The sum over α is such that the only terms that are included are those for which $\Delta_b < \Delta_{\alpha}(\mathbf{k}) < \Delta_F$, and the wave functions are evaluated for $\Delta = \Delta_{\alpha}(\mathbf{k})$. The matrix $Q^{\alpha n}$ in this equation is the product of \underline{F}^{α} and \underline{S}^n . This expression has the usual advantage obtained from a Green-function formulation, there is no need to normalize the wave functions $\phi_L^{\Delta}(\mathbf{r})$ beyond the application of the condition in (9).

The formula in (33) is completely correct, but it is obvious that there is a practical difficulty that could arise when it is used for calculations. The integral over \mathbf{k} is done by evaluating the contributions for a finite set of \mathbf{k}_i and summing with the help of a weight function $w(\mathbf{k}_i)$. It might be thought that it would be very unlikely that a $\Delta_{\alpha}(\mathbf{k}_i)$ would equal a Δ_n^s to such an accuracy that the denominator in (33) would appear to be zero to the machine. Unfortunately, there are usually one or two zeros of the sine matrix in the range of energies covered by the band, and many eigenvalues are generated in the process of iterating to self-consistency so that this unlikely event happens several times during the course of a band-theory calculation. The contribution to the charge density from the wave function associated with one

$\Delta_\alpha(\mathbf{k}_i)$ is very small, which suggests that a few troublesome points could be identified and simply ignored. Such a procedure works well enough so that reasonable eigenvalues can be obtained, but the step in which the total energy is calculated requires another level of consistency in the calculation of eigenvalues, potentials, and charge densities. After many iterations the calculated total energies continued to oscillate with an amplitude that is small but unacceptable. This is the problem with the formula in (33) that caused the slow down in the development of the QKKR alluded to in the Introduction.

III. REFORMULATION OF THE EQUATION

The resolution of this problem is found with the help of some algebra that starts with the alternative formula for $\phi_L^\Delta(\mathbf{r})$ from scattering theory

$$\phi_L^\Delta(\mathbf{r}) = \sum_{L'} [N_{L'}^\Delta(\mathbf{r}) S_{L'L}^\Delta - J_{L'}^\Delta(\mathbf{r}) C_{L'L}^\Delta], \quad (34)$$

in which $N_L^\Delta(\mathbf{r})$ is the solution of (8) that satisfies the boundary condition

$$\lim_{r \rightarrow \infty} N_L^\Delta(\mathbf{r}) = Y_L(\mathbf{r}) n_l(\kappa_0 r). \quad (35)$$

Inserting (34) into (28) and manipulating the terms leads to

$$\begin{aligned} W_L^\Delta(\mathbf{r}) &= \sum_{L', L''} H_{LL'}^\Delta [(\tilde{C}^\Delta)^{-1}]_{L'L''} \phi_{L''}^\Delta(\mathbf{r}) \\ &\quad - \sum_{L'} [(\tilde{C}^\Delta)^{-1}]_{LL} N_L^\Delta(\mathbf{r}), \end{aligned} \quad (36)$$

where H^Δ is the product of F^Δ and the matrix of KKR structure constants $B(E_0, \mathbf{k})$. The determinant of the cosine matrix is zero for the energies Δ_n^c , so the inverse of that matrix can be written

$$(\underline{C}^\Delta)^{-1} = \sum_n \frac{C^n}{\Delta - \Delta_n^c}, \quad (37)$$

and, from the same arguments that were used before, $\rho(\mathbf{r})$ is obtained by integrating

$$A(\mathbf{k}, \mathbf{r}, \mathbf{r}') = -\kappa_0 \sum_{L, L'} \phi_L^\Delta(\mathbf{r}) \frac{R_{LL'}^{\alpha n}}{\Delta_\alpha(\mathbf{k}) - \Delta_n^c} \phi_{L'}^\Delta(\mathbf{r}'). \quad (38)$$

The matrix $R^{\alpha n}$ is the product of $F^\alpha(\mathbf{k})$, $B(E_0, \mathbf{k})$, and \tilde{C}^n . The comments made after (33) concerning the terms in the sum apply here.

The calculation is done by switching back and forth between the expressions in (33) and (38). If a $\Delta_\alpha(\mathbf{k})$ is too close to a zero of the sine matrix, (38) must be used, while (33) is used otherwise. This process seems a bit labored, but it is quite easy to put into practice. It does not add appreciably to the time required for the calculation. The zeros of the sine cosine matrices, Δ_n^s and Δ_n^c , are not dense in energy, and scattering theory requires that the zeros of the cosine matrix will fall between those of the sine matrix. These quantities do not depend on \mathbf{k} , so the relevant values can be calculated and stored at the beginning of each iteration.

This is the practical resolution of the difficulty in

evaluating the Green function, but it might seem ad hoc. The process can be clarified by noting that $W_L^\Delta(\mathbf{r})$ can be written

$$W_L^\Delta(\mathbf{r}) = \sum_{L'} F_{LL'}^\Delta U_{L'}^\Delta(\mathbf{r}), \quad (39)$$

where

$$U_L^\Delta(\mathbf{r}) = -\sum_{L'} B_{LL'}(E_0, \mathbf{k}) J_{L'}^\Delta(\mathbf{r}) - \kappa_0 N_L^\Delta(\mathbf{r}). \quad (40)$$

It is clear that when this function is used in the formula for the Green function in (27) there will be no problem from the inverse of either a sine or cosine matrix. The formula for the contributions to the charge density is simply

$$A(\mathbf{k}, \mathbf{r}, \mathbf{r}') = \kappa_0 \sum_{\alpha, L, L'} \phi_L^\Delta(\mathbf{r}) F_{LL'}^\alpha U_{L'}^\Delta(\mathbf{r}'), \quad (41)$$

where $\phi_L^\Delta(\mathbf{r})$ and $U_L^\Delta(\mathbf{r})$ are evaluated at $\Delta = \Delta_\alpha(\mathbf{k})$. This formula is not useful because the functions that appear in $U_L^\Delta(\mathbf{r})$ are singular at $r=0$, but it provides the best proof that the problems caused by the inverse of the scattering matrices must be only formal. Equations (28), (36), and (39) are all correct, since (40) may be rewritten

$$\begin{aligned} U_L^\Delta(\mathbf{r}) &= -\kappa_0 \sum_{L'} [(\tilde{S}^\Delta)^{-1}]_{LL} \phi_{L'}^\Delta(\mathbf{r}) \\ &\quad - \sum_{L', L''} D_{LL'}^\Delta [(\underline{S}^\Delta)^{-1}]_{L'L''} J_{L''}^\Delta(\mathbf{r}), \\ U_L^\Delta(\mathbf{r}) &= \sum_{L'} B_{LL'}(E_0, \mathbf{k}) [(\tilde{C}^\Delta)^{-1}]_{L'L''} \phi_{L''}^\Delta(\mathbf{r}) \\ &\quad - \sum_{L', L''} D_{LL'}^\Delta [(\underline{C}^\Delta)^{-1}]_{L'L''} N_{L''}^\Delta(\mathbf{r}). \end{aligned} \quad (42)$$

Inserting these functions into (41) leads to (33) and (38), because the product of F^α with \underline{D}^Δ , the inverse of \underline{F}^Δ , is zero when $\Delta = \Delta_\alpha(\mathbf{k})$.

IV. COMPUTATIONAL RESULTS

The basis for the proposition that the QKKR formalism will give the correct results for full SC potentials follows from the derivation sketched above and the fact that it has already been demonstrated that it yields accurate eigenvalues for SCMT potential.⁴ The function $\Delta\sigma(\mathbf{r})$ in the potential $v^\Delta(\mathbf{r})$ is a larger non-muffin-tin contribution than any difference between a SC and SCMT potential that will arise in practice, so the method would not work at all if non-muffin-tin potentials posed a problem. A numerical demonstration of this proposition is provided by the results of a QKKR calculation of the differences between eigenvalues calculated with two niobium potentials shown in Table I. One of the potentials was generated without a shape approximation and the other was obtained by a muffin-tin truncation of that one. The shifts predicted by the QKKR show the same trends as those calculated with other band-theory methods that are shown in that table. At the present time, it is as reasonable to believe that the QKKR shifts are correct as any of the others.

A calculation of the energy bands of niobium using a

TABLE I. A comparison of the differences between eigenvalues of niobium using a potential with no shape approximation and a potential which is its muffin-tin truncation, as calculated with the QKKR and other band-theory methods. The discrete-variational-method (DVM) calculations are described in Ref. 13, while the ones done with the modified augmented-plane-wave (APW) method are reported in Ref. 14.

| Symmetry | QKKR (mRy) | DVM (mRy) | APW (mRy) |
|----------------|---------------|--------------|--------------|
| Γ_1 | -4.2 | -1.6 | 0.8 |
| Γ_{12} | -10.5 | -9.8 | -13.2 |
| Γ'_{25} | 5.7 | 7.6 | 7.7 |

full SC potential has recently been published by Jani, Brener, and Callaway.¹⁶ They gave a table comparing differences between selected eigenvalues from their calculation with those published by several other groups. We have revised and extended this table by removing two calculations that were done with exchange-only potentials and inserting three QKKR calculations, and the results appear in Table II.

The lattice constant in our SCMT calculation QKKRMT(1), 6.20 a.u., is the same as the one used in the KKR muffin-tin calculations of Moruzzi, Janak, and Williams¹⁷ that appears in the preceding line of Table II. The close agreement between the KKR and QKKRMT(1) energy separations demonstrates the precision of the QKKR when operating in a muffin-tin mode.

The lattice constant used in the QKKR and QKKRMT(2) calculations, 6.227 a.u., is the same as the one used in the linear combination of Gaussian orbitals (LCGO) calculations of Jani, Brener, and Callaway.¹⁶ The agreement between the results of the calculations with full SC potentials using the QKKR and the LCGO is reasonably good, but there are significant differences at the H point. This may be attributable to small differences in the way that the potentials are generated. We used 168 k points in an irreducible $\frac{1}{48}$ wedge of the first Brillouin zone in generating our SC potential.

The lattice constant of 6.236 a.u. was used in the linear combination of muffin-tin orbitals (LMTO) calculation,¹⁸ and the lattice constant used in the mixed-basis pseudo-potential (MBP) calculation¹⁹ is presumably about the

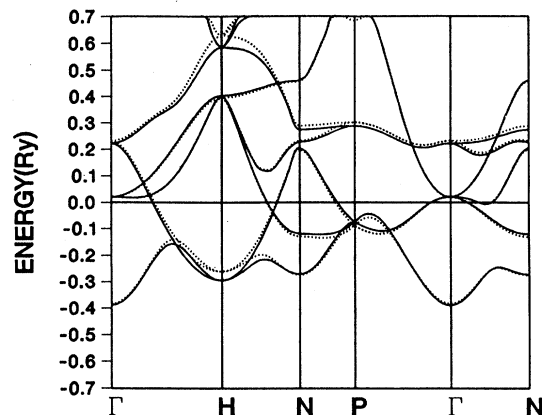


FIG. 1. The energy bands for niobium plotted so that the zero of energy is the Fermi energy. The solid lines show the bands calculated with the QKKR and the full SC potential that led to the eigenvalue separations in the last line of Table II. The dotted lines show the bands for the muffin-tin calculations denoted in the text and Table II as QKKRMT(2).

same as the others. The energy separations calculated with the MBP and LMTO are outside the range established by the other calculations, including the ones done with a muffin-tin approximation.

The SCMT potential used to calculate the energy separations denoted by OKKRMT(2) is defined in the usual way.¹⁷ A comparison of the QKKRMT(2) and QKKR values illustrates the magnitude of the shifts in eigenvalues that can be expected when a muffin-tin or a SC potential is used for niobium. The main shifts are in the eigenvalues at the H point. One reason for focusing on niobium as a test case is that a previous study¹³ demonstrated that the effect on the eigenvalues of this shape approximation is much greater for that metal than for rubidium or palladium, presumably because the Fermi energy falls in the middle of the d bands of niobium.

The energy bands for the full SC potential from which the QKKR energy separations are excerpted are shown in Fig. 1. The occupied bands are almost identical to the LCGO bands in Ref. 16. The small differences are probably more due to draftmanship than anything else. Our curves were drawn by a computer with, for example, 21 points between Γ and H . The Fermi surface dimensions

TABLE II. Selected energy separations (in mRy) of niobium eigenvalues presented in the references cited. The abbreviations are explained in text. All of the calculations use the standard local-density approximation (Ref. 15) for the self-consistent potentials. The LCGO, MBP, LMTO, and QKKR calculations were carried out with no approximation to the shape of the SC potentials.

| Method | $E_{\Gamma'_{25}} - E_{\Gamma_1}$ | $E_{H'_{25}} - E_{\Gamma_1}$ | $E_{H'_{25}} - E_{H_{12}}$ | $E_F - E_{H_{12}}$ | $E_F - E_{\Gamma_1}$ | $E_{N'_1} - E_{\Gamma_1}$ |
|----------------|-----------------------------------|------------------------------|----------------------------|--------------------|----------------------|---------------------------|
| LCGO (Ref. 16) | 404 | 792 | 687 | 282 | 387 | 577 |
| KKR (Ref. 17) | 410 | | | 302 | 387 | |
| QKKRMT(1) | 409 | 799 | 710 | 302 | 389 | 600 |
| MBP (Ref. 18) | 433 | 795 | 613 | 243 | 425 | 570 |
| LMTO (Ref. 19) | 480 | | | 304 | 452 | |
| QKKRMT(2) | 409 | 791 | 698 | 296 | 388 | 594 |
| QKKR | 402 | 777 | 656 | 262 | 382 | 582 |

from the QKKR calculations agree very well with the ones reported in Ref. 16. The bands obtained with the SCMT potential used for the OKKRMT(2) entries in Table II are also shown in Fig. 1. This provides an illustration of the effects of the shape approximation discussed above.

It should be emphasized that all the bands in Fig. 1 were calculated with one value for E_0 . It was not necessary to carry out a number of calculations in energy sub-intervals and put them together in order to cover the energy range shown.

As mentioned earlier, the problem with the zeros of the sine and cosine matrices does not affect the calculation of eigenvalues. Total-energy calculations are affected, but, using the new formulas, agreement has been found with the total energies reported by Moruzzi, Janak, and Williams¹⁷ to within one or two millirydbergs.

These calculations go even faster than might be expected from a casual perusal of (33) and (38). All of the quantities that are needed can be calculated using power-series expansions in Δ . Even the $\phi_L^\Delta(\mathbf{r})$ are evaluated for the necessary values of $\Delta_\alpha(\mathbf{k})$ using functions that are calculated at the beginning of each iteration.

V. DISCUSSION

Self-consistent QKKR band-theory calculations can now be done for fcc and bcc lattices with full SC potentials. Total-energy calculations are working well for SCMT potentials, but we are not confident about the results of our total-energy calculations for SC potentials at the present time. We are convinced that the differences in the total energies of materials in different crystalline

phases are meaningful only when they are calculated with the full potential, so we consider the extension of our total-energy programs to the SC case to be a high priority.

Another development that will be very useful is the ability to do impurity calculations. Our algebraic studies indicate that the QKKR has advantages in this type of calculation. One advantage that it has over previous treatments of this problem is that it is not restricted to SCMT potentials. For this reason, we can calculate heats of solution with some confidence. These calculations will be relatively fast because many operations that are quite complicated in other approaches are replaced by manipulations of finite matrices.

It is desirable to develop the necessary extensions of the QKKR so that lattices with many atoms per unit cell can be treated, and to include relativity and magnetism. Now that the simpler calculations are going well, we are encouraged to move into these areas.

The solution of these problems will help us attain our goal of using quantum-mechanical calculations to design new materials.

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