Multiple-scattering approach to band theory. II. Fast band theory

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The multiple-scattering equations are used to derive a set of band-theory equations that are called the pivoted-multiple-scattering (PMS) equations. The PMS equations are as legitimate a basis for band-theory calculation as the Korringa-Kohn-Rostoker (KKR) equations that are also derived from the multiple-scattering theory. The primary usefulness of the PMS equations is that an approximate expression can be derived from them that gives all the eigenvalues for one $\vec{k}$ with a single-matrix diagonalization. This expression has the form of a quadratic eigenvalue equation. The usefulness and accuracy of this quadratic KKR formalism is demonstrated by a number of numerical studies.

I. INTRODUCTION

In this paper a new band-theory equation for calculating electronic-energy eigenvalues and wave functions for periodic solids is derived from multiple-scattering theory.[1] Over the range of energies that is of interest, the eigenvalues that are calculated from this equation are essentially equal to the ones obtained from fully converged Korringa-Kohn-Rostocker (KKR) calculations.[2,3] However, all of the eigenvalues for a given $\vec{k}$ vector are obtained by diagonalizing one matrix, while the determinants of many matrices would have to be evaluated in order to find the same eigenvalues with the KKR equations. Since it takes about the same amount of time to find the determinant as to diagonalize a matrix, band-theory calculations may be carried out with this new equation in a small fraction of the time that would be reguired if the KKR equation was used. Certain types of theoretical calculations, particularly those that require the evaluation of the total energy of the solid, become more feasible with this new equation.

A number of band-theory methods have been proposed in recent years that attempt to combine the accuracy and generality of the first-principles band-theory methods [KKR, augmented plane wave (APW)] with the computational ease of simple tight-binding models. These methods are called linearized band theories because they reformulate the problem in such a way that the elements of the secular matrix, which have a complicated energy dependence in the first-principles methods, are replaced by elements that depend linearly on E. The energy eigenvalues for which the determinant of the secular matrix is zero may obviously be found by diagonalization. These linearized theories are

Rayleigh-Ritz variational calculations in which the first-principles methods are used as a guide to the choice of efficient trial functions. In a previous paper,[4] which will be called I, it was shown that a band-theory equation can be derived from multiple-scattering theory that has the property of the elements of the secular matrix are a rapidly convergent power series in energy. A linearized version of this equation was compared in detail with some of the better-known linearized band theories.[5] In the present paper it is shown that the inclusion of the quadratic terms in the elements of the secular matrix leads to a considerable improvement in the accuracy of the calculations. The eigenvalues calculated from a secular matrix that is quadratic in energy can also be found by diagonalization. This is the feature that speeds up the calculations, and it is not unique to linearized theories. For this reason, this class of band-theory equations are referred to as fast band theories.

In the next section a pivoted-multiple-scattering (PMS) band-theory equation is derived. It is illustrated with the aid of calculations on real solids. The PMS idea was proposed in I, but a number of approximations were made at an early stage of the theory. The power of the PMS equation is illustrated much better by the present calculations in which the number of additional approximations is held to a minimum. The greatest gain in accuracy is achieved by using the actual shape of the unit cell, rather than a spherical model, in calculating the scattering matrices.

Band-theory calculations done with the PMS equation are as time consuming as calculations done with the KKR equation, even though the energy dependence of the structure constants has been eliminated. The primary advantage of the

PMS equation is that it provides a convenient basis for deriving fast-band-theory equations. This derivation is carried out in Sec. III. It is shown in that section that the secular matrix that appears in the formulation can be approximated very accurately as quadratic functions of energy over the range of energies that are of interest in band-theory calculations. It is this fact that leads to the conclusion that a quadratic band-theory equation should be useful. This quadratic band-theory equation, called the QKKR equation, is investigated both algebraically and numerically. The advantage that it has over a linear equation is shown by calculation. An optimized scheme is developed for the implementation of this equation in self-consistent total-energy calculations for solids. The results are summarized and commented upon in Sec. IV.

It should be pointed out that the motivation for this development is the desire to calculate the total energies of transition metals more rapidly and accurately than can be done with any formalism that was previously available. The form that the equations take is affected to some extent by this goal. The development is quite general though, and modifications of these equations can be worked out for other applications.

II. PIVOTED-MULTIPLE-SCATTERING THEORY

According to the density-functional theory,[6] the electronic states in a solid can be accurately described in terms of one-electron Bloch functions $\psi_{\vec{k}}^{\alpha}(\vec{r})$ that are the bounded solutions of

$$[-\nabla^2 + V(\vec{r})]\psi_{\vec{k}}^{\alpha}(r) = E^{\alpha}(\vec{k})\psi_{\vec{k}}^{\alpha}(\vec{r}) . \tag{1}$$

The eigenvalues and eigenfunctions are, as usual, denoted by Bloch vectors $\vec{k}$ and band indices α. The one-electron potential $V(\vec{r})$ is a single-valued function of $\vec{r}$ that has the periodicity of the crystal. Thus,

$$V(\vec{r} + \vec{R}_n) = V(\vec{r}) , \tag{2}$$

for any lattice vector $\vec{R}_n$. From this it follows that $V(\vec{r})$ can always be written as a sum of identical potentials centered at the various lattice points

$$V(\vec{r}) = \sum_n v(\vec{r} - \vec{R}_n) . \tag{3}$$

If the solid is assumed to have one atom per unit cell (the generalization to other cases is straightforward), the potential $v(\vec{r} - \vec{R}_n)$ describes the scattering of the electron from the atom on the nth site. The derivation of the standard multiple-scattering

equations from the Lippmann-Schwinger equation can be carried out only if these atomic potentials do not overlap. That is, the potentials $v(\vec{r} - \vec{R}_n)$ are defined as function of $\vec{r}$ within regions Ω_n centered on the sites $\vec{R}_n$. The boundaries of the regions Ω_n corresponding to neighboring sites must not touch. $V(\vec{r})$ is a constant in the intersitial region between the Ω_n.

By definition, the region Ω_n fits within the nth unit cell. There are many ways to construct a unit cell, but we use the Wigner-Seitz cell, which is the most symmetrical. The radius of the smallest sphere within which the region Ω_n can be fitted will be called S. If the muffin-tin approximation is used, S is equal to the muffin-tin radius r_{mt}, which is the radius of the largest sphere that can be inscribed in the Wigner-Seitz cell. For the most general non-muffin-tin potential, the boundary of the region Ω_n will differ only infinitesimally from the boundary of the Wigner-Seitz cell. For this case S is the radius of the smallest sphere that can be circumscribed about the Wigner-Seitz cell.

In I, it was shown using multiple-scattering theory that for a general potential $V(\vec{r})$ the eigenfunctions $\psi_{\vec{k}}^{\alpha}(\vec{r})$ can be written

$$\psi_{\vec{k}}^{\alpha}(\vec{r}) = \sum_L Z_L(E^{\alpha}(\vec{k}), \vec{r})C_L^{\alpha}(\vec{k}) . \tag{4}$$

In this expression, $Z_L(E, \vec{r})$ is a solution of the differential equation

$$[-\nabla^2 + v(\vec{r})]f(E, \vec{r}) = Ef(E, \vec{r}) . \tag{5}$$

It is the solution that for $r > S$ satisfies the boundary condition

$$Z_L(E, \vec{r}) = \kappa Y_L(\vec{r})n_l(\kappa r) - \sum_{L'} Y_{L'}(\vec{r})j_{l'}(\kappa r)X_{L'L}(E) , \tag{6}$$

in which κ is the square root of E, $j_l(\kappa r)$ and $n_l(\kappa r)$ are Bessel functions, $Y_L(\vec{r})$ are real spherical harmonics, and L stands for the two integers l and m. The matrix $\underline{X}(E)$ is minus the inverse of the Wigner scattering matrix, $\underline{R}$, that describes the scattering of an electron of energy E from the potential $v(\vec{r})$. Hence, it is both real and symmetrical. The coefficients $C_L(\vec{k})$ are shown in I to be solutions of a homogeneous set of equations

$$\sum_{L'} M_{LL'}(E, \vec{k})C_{L'}(\vec{k}) = 0 . \tag{7}$$

Obviously, these equations have nontrivial solutions only for energies $E^{\alpha}(\vec{k})$ for which

$$\det \underline{M}(E, \vec{k}) = 0 . \tag{8}$$

The matrix $\underline{M}(E, \vec{k})$ can be written in the form

$$\underline{M}(E, \vec{k}) = \underline{X}(E) + \hat{\underline{B}}(E, \vec{k}) , \tag{9}$$

where $\underline{X}(E)$ is the scattering matrix described above and $\widehat{B}(E,\vec{k})$ is a symmetrical matrix of elements called structure constants.

For the special case that the bounding spheres of the regions Ω_n do not overlap, the elements of $\widehat{B}(E,\vec{k})$ go over to the KKR structure constants defined originally by Korringa.[7] The KKR structure constants $B_{LL'}(E,\vec{k})$ do not depend at all on the potentials, but only on the crystal structure. The differences

$$N_{LL'}(E,\vec{k})=\widehat{B}_{LL'}(E,k)-B_{LL'}(E,\vec{k}) , \qquad (10)$$

are called the near-field corrections to the structure constants. From the defining equation in I it is clear that the $N_{LL'}(E,\vec{k})$ do depend on $v(\vec{r})$. A further specialization of the band-theory equations arises when the potentials $v(\vec{r})$ are spherically symmetric. This simplification has the effect of making the scattering matrix $\underline{X}(E)$ diagonal. In fact, the matrix elements for this case are simply

$$X_{LL'}(E)=\kappa \cot\eta_l(E)\delta_{LL'} , \qquad (11)$$

where the $\eta_l(E)$ are the phase shifts that describes the scattering of an electron from the spherical potential. The well-known muffin-tin form for the potential that is assumed in most papers on the KKR method corresponds to the case that the $v(\vec{r}-\vec{R}_n)$ are spherically symmetric and their bounding spheres do not overlap.

It was pointed out in I that the most convenient form for $\underline{X}(E)$ for a general $v(\vec{r})$ is

$$\underline{X}=\kappa\underline{C}\,\underline{S}^{-1} , \qquad (12)$$

where $\underline{C}(E)$ is a generalized cosine matrix and $\underline{S}(E)$ is a generalized sine matrix. Several expressions for evaluating the elements of these matrices are given in I, and it is shown that for spherical potentials they go over to

$$C_{LL'}(E)=A_l\cos\eta_L(E)\delta_{LL'} ,$$
$$S_{LL'}(E)=A_l\sin\eta_l(E)\delta_{LL'} . \qquad (13)$$

It follows from (6) that for any energy for which the determinant of the sine matrix is zero (or a phase shift is zero in the spherical case) the normalization of $Z_L^\alpha(E,\vec{r})$ becomes infinite. This is an inconvenience which can be eliminated by expressing $\psi_{\vec{k}}^\alpha(\vec{r})$ in terms of the functions

$$\phi_L(E,\vec{r})=\frac{1}{\kappa}\sum_{L'}Z_{L'}(E,\vec{r})S_{L'L}(E) . \qquad (14)$$

These functions are also real solutions of (5), and can be shown to have the normalization

$$\lim_{r\to 0}\phi_L(E,\vec{r})=Y_L(\vec{r})j_l(\kappa r) , \qquad (15)$$

which is finite for any finite E. The coefficients $d_L(\vec{k})$ in

$$\psi_{\vec{k}}^\alpha(\vec{r})=\sum_L \phi_{L'}(E^\alpha(\vec{k}),\vec{r})d_L^\alpha(\vec{k}) \qquad (16)$$

satisfy the set of equations

$$\sum P_{LL'}(E,\vec{k})d_{L'}(\vec{k})=0 , \qquad (17)$$

in which the matrix $\underline{P}(E,\vec{k})$ is

$$\underline{P}(E,\vec{k})=\underline{M}(E,\vec{k})\underline{S}(E) . \qquad (18)$$

This unsymmetrical matrix is the most useful one to consider in the multiple-scattering approach to band theory because it remains finite for all energies, and, unlike the symmetrical matrix $\widetilde{\underline{S}}\,\underline{M}\,\underline{S}$, the only energies for which its determinant is zero are the $E_\alpha(\vec{k})$.

The band-theory equations (16)—(18) are straightforward generalizations of the ones derived with multiple-scattering theory by Korringa.[2] They were recast, without approximation, into an equivalent form in I. The new form seems a bit curious at first sight, but it proves to be useful for later derivations. In the process of defining the potential $V(\vec{r})$ it was pointed out that the regions Ω_n without which the $v(\vec{r}-\vec{R}_n)$ are defined do not touch, and that the potential $V(\vec{r})$ is a constant in the interstitial region between the Ω_n. All of the energies in (16)—(18) are defined relative to this constant, so it has tacitly been assumed to be zero. For the most general non-muffin-tin potential the boundaries of the regions Ω_n approach the boundaries of the Wigner-Seitz cells, and the volume of the interstitial region goes to zero. For this case the value of the constant interstitial potential becomes an irrelevant parameter. By choosing a value other than zero for this parameter, it is possible to recast (16)—(18) into the new form.

The scattering matrix $\underline{X}(E)$ describes the scattering of an electron with an energy E from the potential $v(\vec{r})$ that is assumed to be zero outside the region Ω_0. If the potential outside Ω_0 is assigned the new value $E-E_0$, then the incoming electron will appear to have the energy E_0 and the scattering is described by the matrix $\underline{X}^\Delta(E_0)$. This matrix can be calculated equally well by considering an electron traveling in a region of zero potential with energy E_0 and then scattering from the potential

$$v^\Delta(\vec{r})=v(\vec{r})-\Delta\sigma(\vec{r}) , \qquad (19)$$

where $\Delta=E-E_0$. The function $\sigma(\vec{r})$ is a step function that is equal to one when $\vec{r}$ is inside Ω_0 and zero when it is outside. For the reasons outlined above, the scattering matrix $\underline{X}^\Delta(E_0)$ can be

used in new band-theory equations if the region Ω_0 is the Wigner-Seitz cell. Let $\phi_L^\Delta(E_0,r)$ be the solution of an equation like (5) but with $v(\vec{r})$ replaced by $v^\Delta(\vec{r})$. It satisfies the condition

$$\lim_{r \to 0} \phi_L^\Delta(E_0,\vec{r}) = Y_L(\vec{r})j_l(\kappa_0 r) , \tag{20}$$

with κ_0 equal to the square root of E_0. It can be seen that the Bloch vector in (16) can be written

$$\psi_{\vec{k}}^\alpha(\vec{r}) = \sum_L \phi_L^{\Delta_\alpha(\vec{k})}(E_0,\vec{r})\hat{d}_L^\alpha(\vec{k}) , \tag{21}$$

where the coefficients $\hat{d}_L^\alpha(\vec{k})$ are solutions of the set of equations

$$\sum P_{LL'}^\Delta(E_0,\vec{k})\hat{d}_{L'}(\vec{k}) = 0 , \tag{22}$$

in which

$$\underline{P}^\Delta(E_0,\vec{k}) = \kappa_0 \underline{C}^\Delta(E_0)$$
$$+ [\underline{B}(E_0,\vec{k}) + \underline{N}^\Delta(E_0,\vec{k})]\underline{S}^\Delta(E_0) . \tag{23}$$

The sine and cosine matrices are defined so that

$$\underline{X}^\Delta(E_0) = \kappa_0 \underline{C}^\Delta(E_0)\underline{S}^\Delta(E_0)^{-1} , \tag{24}$$

and there are near-field corrections to the structure constants $\underline{N}^\Delta(E_0,\vec{k})$ whether $v(\vec{r})$ is of the muffin-tin form or not because of the second term in $v^\Delta(\vec{r})$. Nontrivial solutions of (22) exist only for those values of Δ for which the determinant of $\underline{P}^\Delta(E_0,\vec{k})$ is zero. We called them $\Delta_\alpha(\vec{k})$ in (21), and the ordinary energy eigenvalues can be found from

$$E_\alpha(\vec{k}) = \Delta_\alpha(\vec{k}) + E_0 . \tag{25}$$

This set of band-theory equations is entirely equivalent to the ones in (16)—(18), the only difference being that the variable is the depth of the potential rather than the energy of the electron.

We call the band-theory equations (21)—(23) the pivoted-multiple-scattering (PMS) equations because of the appearance of the pivotal energy E_0. In their exact form they are more cumbersome to deal with computationally than the KKR equations [(16)—(18)]. They become very much easier to deal with if we can ignore the near-field corrections to the structure constants, and in all of the following work we make the approximation

$$\underline{N}^\Delta(E_0,\vec{k}) = 0 . \tag{26}$$

After this approximation, the only energy dependence in the secular matrix $P^\Delta(E_0\vec{k})$ defined in (23) comes from the scattering matrices $\underline{C}^\Delta(E_0)$ and $\underline{S}^\Delta(E_0)$. Recall that $\underline{B}(E_0,\vec{k})$ is a matrix

whose elements are the usual KKR structure constants[7] calculated for the pivotal energy and various $\vec{k}$.

The equations from I that we have found to be the most useful for calculating the nondiagonal sine and cosine matrices are

$$C_{LL_0}^\Delta(E_0) = \kappa_0 \int n_l(\kappa_0\vec{r})Y_L(\vec{r})v^\Delta(\vec{r})$$
$$\times \phi_{L_0}^\Delta(E_0,\vec{r})\,dv - \delta_{LL_0} ,$$
$$S_{LL_0}^\Delta(E_0) = \kappa_0 \int j_l(\kappa_0\vec{r})Y_L(\vec{r})v^\Delta(\vec{r}) \tag{27}$$
$$\times \phi_{L_0}^\Delta(E_0,\vec{r})\,dv .$$

These equations are essentially the same as some described by Calogero,[8] except for a minus sign. The function $\phi_L^\Delta(E_0,\vec{r})$ is most conveniently found by solving the integral equation

$$\phi_{L_0}^\Delta(E_0,\vec{r}) = Y_{L_0}(\vec{r})j_{l_0}(\kappa_0 r)$$
$$+ \int_{|\vec{r}'| \leq |\vec{r}|} \widetilde{G}(E_0,\vec{r},\vec{r}')v^\Delta(r')$$
$$\times \phi_{L_0}^\Delta(E_0,\vec{r}')\,dv , \tag{28}$$

in which

$$\widetilde{G}(E_0,\vec{r},\vec{r}') = -\kappa_0 \sum_L Y_L(\vec{r})[j_l(\kappa_0 r)n_l(\kappa_0 r')$$
$$- n_l(\kappa_0 r)j_l(\kappa_0 r')]Y_L(\vec{r}') . \tag{29}$$

We have set up computer programs for calculating $\underline{C}^\Delta(E_0)$ and $\underline{S}^\Delta(E_0)$ for fcc and bcc crystals. We have checked the accuracy of the PMS equations by doing PMS calculations with muffin-tin potentials $v(\vec{r})$ for which ordinary KKR calculations can be carried out to great precision. Of course, the sine and cosine matrices must be calculated with (27)—(29) even for a muffin-tin potential because $v^\Delta(\vec{r})$ is not spherically symmetric.

The results of one of our calculations comparing eigenvalues from a PMS calculation with the ones given by a KKR calculation are shown in Fig. 1. A bcc lattice of niobium muffin-tin potentials was used, and angular momenta through $l_{\max}=4$ were included. All of the bands shown in this paper were calculated with this test potential. The energies are all expressed in the dimensionless units (du) that are frequently used in KKR calculations, $E_{\mathrm{du}} = (a/2\pi)^2 E_{\mathrm{Ry}}$, in which a is the lattice constant and E_{Ry} the energy in rydbergs. The energies in this paper can be converted to rydbergs by multiplying with 1.017343. The value of E_0 was chosen to be 0.66955 du. It can be seen that the PMS and KKR eigenvalues are essentially identical
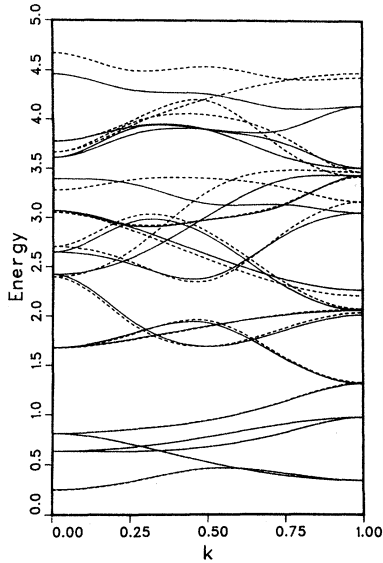
FIG. 1. Energy bands calculated with the KKR equations (solid lines) and with the PMS equations (dashed lines). All of these calculations use l values through $l_{max}=4$. Potential represents niobium atoms on a bcc lattice with lattice constant $a=3.2964$ Å. Energy is expressed in dimensionless units (du) which can be converted to rydbergs by multiplying with 1.017 343. Pivotal energy E_0 is 0.669 55 du.

over the range of energies that are of interest in most band-theory applications, 0.0−1.0 du. Between roughly 1.0 and 3.0 du the differences become perceptible, but the bands predicted by the PMS calculation have the same shape and are only shifted slightly from the correct ones. The differences become greater for eigenvalues larger than 3.0 du, but there is still a clear correspondence between the PMS and KKR bands. It is surprising that the PMS eigenvalues for which Δ is 1.0 or 2.0 du are as good as they are because this means that the nonspherical contribution to the potential $\Delta\sigma(\vec{r})$ has become very large. It could have been imagined that the near-field corrections to the structure constants would have come to play an important role in this energy range. The l convergence of scattering matrices can also be a problem for highly anisotropic potentials. This should be a bigger problem for the PMS than the KKR calculations since the test potential always looks spherical to the incoming electron in the KKR approach.

The PMS calculations shown in Fig. 1 are no easier to do than the KKR calculations. Their importance lies in the fact that they provide a starting point for further approximations that do lead to computational schemes that are dramatically

faster than the conventional ones. These will be developed in the next section. Before proceeding with those developments, it is useful to investigate other aspects of the PMS equation numerically.

In Fig. 2, PMS and KKR eigenvalues are compared over the range of energies that are usually of interest in band-theory calculations. They were calculated with the same niobium potential as the eigenvalues in Fig. 1, but the pivotal energy E_0 in the PMS calculations is 0.010 du rather than 0.669 55 du. The PMS eigenvalues are not quite as good in Fig. 1, but they are quite satisfactory. In the same figure are shown eigenvalues calculated with an approximation to the PMS equations in which the polygonal Wigner-Seitz cell is approximated by a Wigner-Seitz sphere. This means that the step function $\sigma(\vec{r})$ in (19) is replaced by a spherically symmetric function $\sigma_{WS}(\vec{r})$ defined by

$$\sigma_{WS}(\vec{r})=\begin{cases}1, & |\vec{r}|\leq r_{WS}\\0, & |\vec{r}|>r_{WS}\end{cases} \tag{30}$$

where r_{WS} is the radius of the Wigner-Seitz sphere. The scattering matrices are diagonal for this case, and their elements can be calculated from formulas that are simpler than (27)−(29). This spherical model was the only one considered in I, and it was
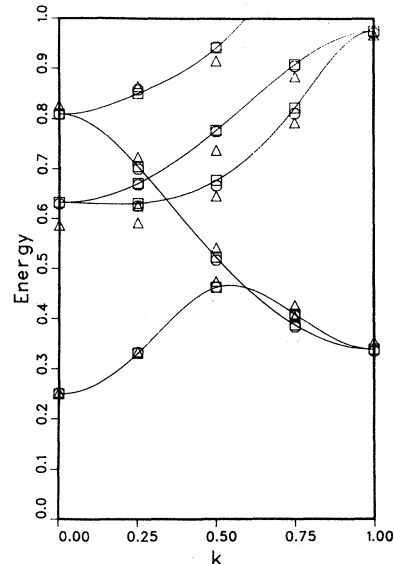

FIG. 2. Niobium eigenvalues in du calculated with the KKR equations (squares), the PMS equations (circles), and the spherical approximation to the PMS equation (triangles). Pivotal energy is $E_0=0.01$ du and $l_{max}=4$. Solid line connects the exact eigenvalues $E_\alpha(\vec{k})$ calculated with the KKR.

discussed by Anderson[9] for the case in which E_0 is zero. It can be seen that for the bcc lattice used in these calculations the spherical model gives the wrong splitting for the d states at $k=0.0$. Eigen-values from calculations that are the same as the ones in Fig. 2 except that E_0 is 0.725 du rather than 0.010 du are shown in Fig. 3. The PMS eigenvalues are essentially identical with the KKR eigenvalues, and the eigenvalues calculated with the spherical model give a much better representation of the d bands. In Fig. 4 are shown eigenvalues calculated as in Fig. 2 except that angular momenta are included only for $l \leq 3$ rather than $l \leq 4$. The improvement that is obtained by including the shape of the unit cell properly in the scattering matrix calculation is clearly less for this case.

The lessons learned from the calculation we have done using the PMS equations (21)—(23) can be summarized as follows. At least for the metallic systems that we have considered, the neglect of the near-field corrections to the structure constants as indicated by (26) introduces very little error in the eigenvalues. The eigenvalues calculated with PMS equations in which the correct nondiagonal sine and cosine matrices defined in (27)—(29) are used are much better than the ones calculated using the spherical approximations to $\sigma(\vec{r})$ indicated in (30) when enough terms are included in the angular momentum expansions, $l_{max} \geq 4$. The spherical approximation introduces smaller errors if E_0 is
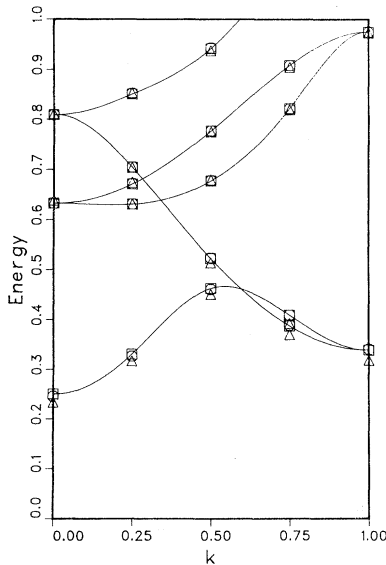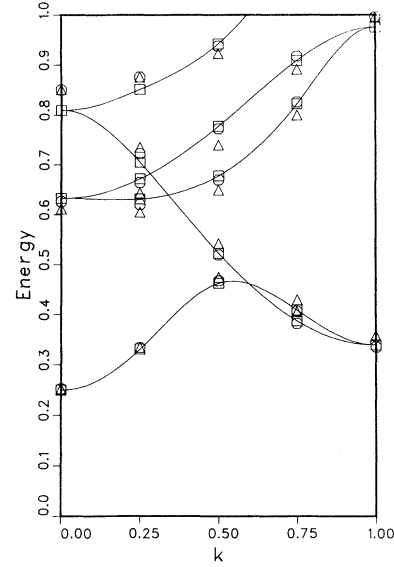

FIG. 4. Niobium eigenvalues calculated with PMS equations (circles) and the spherical approximation to the PMS (triangles) for $E_0=0.010$ du. Calculations differ from the ones in Fig. 2 in that l values are included only through $l_{max}=3$. Squares and solid lines indicate KKR eigenvalues calculated for $l_{max}=4$.

chosen to be in the middle of the d bands. Although we have not shown any examples, the calculation of $\underline{C}^{\Delta}(E_0)$ and $\underline{S}^{\Delta}(E_0)$ is no harder for a non-muffin-tin $v(\vec{r})$ than it is for a muffin-tin potential because the nondiagonal terms are already being included. Finally, we illustrated all of these points for a bcc lattice because the errors caused by a particular approximation are always considerably larger for that lattice than they are for examples in which the fcc lattice is used.

III. FAST BAND THEORIES

By iterating the integral equation (28) and inserting the result in (26) it can be proved that every element of the matrices $\underline{C}^{\Delta}(E_0)$ and $\underline{S}^{\Delta}(E_0)$ is an entire function of Δ. This simply means that these matrix elements can be expanded as Taylor series in Δ, so that

$$\underline{C}^{\Delta}(E_0) = \underline{C}^{(0)}(E_0) + \underline{C}^{(1)}(E_0)\Delta$$
$$+ \underline{C}^{(2)}(E_0)\Delta^2 + \cdots ,$$

$$\underline{S}^{\Delta}(E_0) = \underline{S}^{(0)}(E_0) + \underline{S}^{(1)}(E_0)\Delta$$
$$+ \underline{S}^{(2)}(E_0)\Delta^2 + \cdots .$$

(31)

FIG. 3. Niobium eigenvalues calculated with KKR, PMS, and spherical PMS equations as in Fig. 2, except that $E_0=0.725$ du.

Inserting these expansions in (23) with the approximation (26) leads to

$$\underline{P}^\Delta(E_0,\vec{k}) = \underline{H}(\vec{k}) - \underline{Q}(\vec{k})\Delta + \underline{A}(\vec{k})\Delta^2 + \cdots ,$$

(32)

with

$$\underline{H}(\vec{k}) = \kappa_0\underline{C}^{(0)}(E_0) + \underline{B}(E_0,\vec{k})\underline{S}^{(0)}(E_0) ,$$

$$\underline{O}(\vec{k}) = -\kappa_0\underline{C}^{(1)}(E_0) - \underline{B}(E_0,\vec{k})\underline{S}^{(1)}(E_0) ,$$

(33)

$$\underline{A}(\vec{k}) = \kappa_0\underline{C}^{(2)}(E_0) + \underline{B}(E_0,\vec{k})\underline{S}^{(2)}(E_0) .$$

If all terms beyond the first two in (32) can be ignored, we have what could be called a linearized KKR (LKKR) band theory. The eigenvalues $\Delta_\alpha(\vec{k})$ for which the determinant of $\underline{P}^\Delta(E_0,\vec{k})$ is zero are approximated in this theory by the elements obtained by diagonalizing the matrix

$$\underline{\epsilon}(\vec{k}) = \underline{Q}(\vec{k})^{-1}\underline{H}(\vec{k}) .$$

(34)

The true eigenvalues $E_\alpha(\vec{k})$ that have values very close to E_0 will, of course, be given exactly by the LKKR theory because (26) is satisfied and the higher-order terms in (32) can be ignored as Δ approaches zero. We will show by numerical examples how the approximate eigenvalues from the LKKR are poorer approximations to the exact $E_\alpha(\vec{k})$ when $|E_\alpha(\vec{k})-E_0|$ becomes large. The LKKR band theory was compared in I with the linearized band theories that are derived from a combination of multiple-scattering theory and the Rayleigh-Ritz method.[5] There are many differences, but one of the more important features that distinguishes the equations derived from the pure multiple-scattering approach from the other theories is that the matrices in the LKKR are unsymmetrical. The matrices $\underline{H}(\vec{k})$ and $\underline{Q}(\vec{k})$ would be Hamiltonian and overlap matrices in a variational approach, and they would always be symmetrical. The mathematical consequence of this lack of symmetry is that some of the elements obtained by diagonalizing $\underline{\epsilon}(k)$ are complex. These elements always appear as complex conjugate pairs, and they do not lead to any difficulties in the practical application of the LKKR. The major benefit that arises from the use of these unsymmetrical matrices is that E_0 can be chosen to have any value, and thus one can match to the exact KKR results at the most convenient energy for any application. Also, there is an overall improvement in the quality of the approximation.

An even more striking difference between (32) and equations derived with the variational method is that there is no necessity to stop with a linear-

ized theory. The multiple-scattering formalism leads in a natural way to the inclusion of terms that are quadratic, cubic, quartic, etc., in Δ. In Fig. 5 we compare eigenvalues calculated using a linear and a quadratic approximation to (32) with exact KKR eigenvalues. The calculations were done with the bcc niobium potential used in the preceding examples. Angular momenta were included up to $l_{max} = 4$. As expected, both approximations give very good results near E_0, which for this case has the value 0.669 55 du. Eigenvalues that differ from E_0 by more than a few tenths of a du are given rather badly by the LKKR, but the version of (32) that includes terms quadratic in Δ reproduces the eigenvalues almost exactly over the whole range of energies shown. The additional improvement obtained by including cubic and quadratic terms in (31) would not be worth the effort in most cases.

The quadratic Korringa-Kohn-Rostoker (QKKR) equations are Eqs. (21), (22), and the quadratic form of (32). QKKR calculations, like LKKR calculations, require the diagonalization of just one matrix for each $\vec{k}$. The reduction of a set of equations quadratic in Δ to a set linear in Δ uses a trick that is well known to applied mathematicians. In the present context the transformation is carried out as follows. Equations (22) and (32) are written in the matrix form
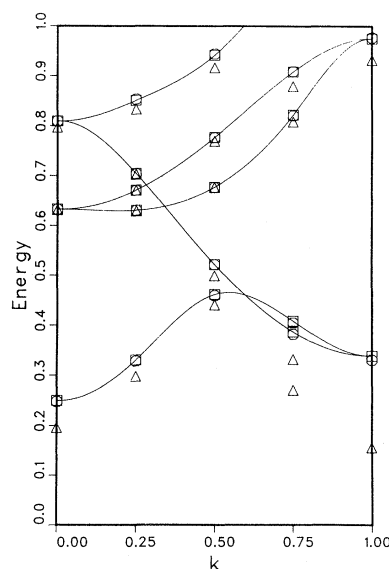

FIG. 5. Niobium eigenvalues calculated with the quadratic (circles) and linear (triangles) approximations with $E_0 = 0.669\ 55$ du. Squares and solid lines are exact KKR bands. Values of l through $l_{max} = 4$ are used in all calculations.

$$[\Delta^2 - \underline{D}(\Delta - \underline{\epsilon})]\underline{d} = 0 , \tag{35}$$

in which $\underline{\epsilon}(k)$ is given by (34) and $\underline{D}(\vec{k})$ is

$$\underline{D}(\vec{k}) = \underline{A}(\vec{k})^{-1}\underline{Q}(\vec{k}) . \tag{36}$$

The elements of the column matrix $\underline{d}(\vec{k})$ are the coefficients $\hat{d}_L(\vec{k})$. A column matrix $\underline{c}$ with elements that will be called $\hat{c}_L(\vec{k})$ is defined by

$$(\Delta - \underline{\epsilon})\underline{d} = \underline{c} . \tag{37}$$

Coupling this equation with one that can be obtained by inserting this definition into (34) leads to a matrix equation that can be written as

$$\begin{bmatrix} \Delta + \underline{\epsilon} + \underline{D} & \underline{\epsilon}^2 \\ -I & \Delta - \underline{\epsilon} \end{bmatrix} \begin{bmatrix} \underline{c} \\ \underline{d} \end{bmatrix} = 0 . \tag{38}$$

This expression has the form of a standard eigenvalue problem. If contributions to the expansion of the wave function in (21) corresponding to angular momenta greater than some l_{max} are ignored, the matrices $H(\vec{k})$, $O(\vec{k})$, and $A(\vec{k})$ will have dimension N, where

$$N = (2l_{max} + 1)^2 . \tag{39}$$

The matrix that must be diagonalized to find the eigenvalues from (38) has dimension $2N$.

The reason that the QKKR gives eigenvalues that agree with the exact results much better than the LKKR is illustrated in Figs. 6 and 7. The averages of the diagonal elements of the cosine matrix corresponding to $l = 1$ and 2 are calculated from (27) for a number of values of Δ. They are plotted in Figs. 6 and 7 as functions of E rather than Δ to facilitate comparison with the eigenvalue calculations. The pivotal energy E_0 is 0.669 55 du, and the same niobium potential is used as in the other examples. The quadratic and linear approximations to these parts of the cosine and sine matrix are plotted in the same figures. The elements of these matrices vary smoothly with Δ, although they are certainly not linear functions of Δ. From these figures it can be seen that the importance of the quadratic approximation lies in the fact that it gives a very good representation of the sine and cosine matrices over a range of energies (of the order 1.0 du) that includes all of the eigenvalues that are of interest in most band-theory calculations.

Another point that is illustrated by comparing Fig. 7 with Fig. 6 is that it is more difficult to fit the components of the cosine and sine matrices for $l = 2$ than for $l = 1$. This is caused by the fact that there is a scattering resonance in the $l = 2$ channel for a transition metal such as niobium. Of all the
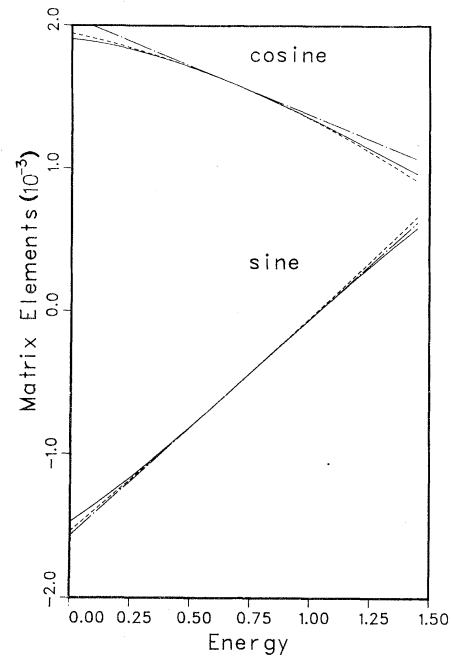

FIG. 6. Average of the $l = 1$ matrix elements of the sine and cosine matrices as a function of energy (solid lines). Quadratic approximation is shown by the dashed lines and the linear approximation by the dotted lines.
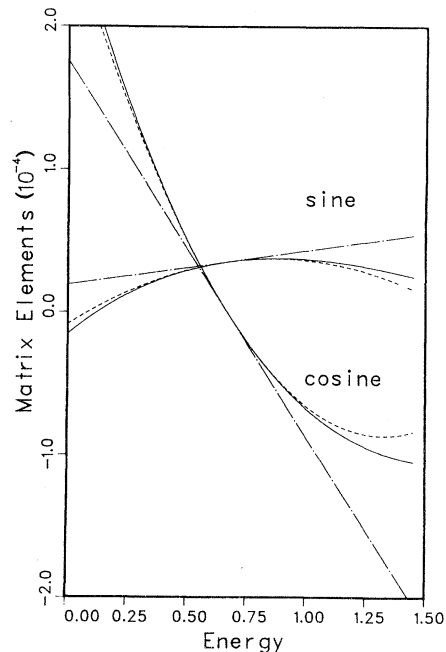

FIG. 7. Average of the $l = 2$ matrix elements of the sine and cosine matrices are shown by solid lines. Quadratic approximation (dashed lines) and linear approximation (dotted lines) are also shown.

matrix elements $C_{LL'}^{\Delta}(E_0)$, these are the ones that will vary most rapidly with Δ. We have found by experience that the best results in either a PMS or QKKR calculation of the eigenvalues for a transition metal are obtained by choosing E_0 to be at or at least near the resonance energy for scattering. The niobium potential we have been using has an $l=2$ scattering resonance at 0.669 55 du, and that is the reason we have used this value for E_0 in many of our calculations.

Eigenvalues calculated for niobium with the QKKR and the LKKR are compared with exact KRR eigenvalues in Fig. 8 for $E_0=0.300$ du. As would be expected, the lowest band is reproduced better for this E_0 than it is for $E_0=0.669\,55$ du. The d bands are given rather badly, however, particularly by the LKKR. The main reason for this is that the parts of the cosine and sine matrices corresponding to $l=2$ are not well reproduced over a wide range of energies by (31) when $E_0=0.300$ du.

Of course, the sine and cosine matrices can be expanded about values other than $\Delta=0$. If they are expanded about Δ_v^0, which is defined by

$$\Delta_v^0 = E_v - E_0 , \tag{40}$$

then (31) takes the form

$$\underline{C}^{\Delta}(E_0) = \underline{C}_v^{(0)}(E_0) + \underline{C}_v^{(1)}(E_0)\Delta_v$$
$$+ \underline{C}_v^{(2)}(E_0)\Delta_v^2 + \cdots ,$$
$$\underline{S}^{\Delta}(E_0) = \underline{S}_v^{(0)}(E_0) + \underline{S}_v^{(1)}(E_0)\Delta_v \tag{41}$$
$$+ \underline{S}_v^{(2)}(E_0)\Delta_v^2 + \cdots ,$$

in which

$$\Delta_v = \Delta - \Delta_v^0 = E - E_v . \tag{42}$$

The expansion of the matrix $\underline{P}^{\Delta}(E_0, \vec{k})$ may be written in terms of these matrices:

$$\underline{P}^{\Delta}(E_0, \vec{k}) = \underline{H}_v(\vec{k}) - \underline{Q}_v(\vec{k})\Delta_v$$
$$+ \underline{A}_v(\vec{k})\Delta_v^2 + \cdots , \tag{43}$$

with

$$\underline{H}_v(\vec{k}) = \kappa_0\underline{C}_v^{(0)}(E_0) + \underline{B}(E_0, \vec{k})\underline{S}_v^{(0)}(E_0) ,$$

$$\underline{Q}_v(\vec{k}) = -\kappa_0\underline{C}_v^{(1)}(E_0) - \underline{B}(E_0, \vec{k})\underline{S}_v^{(1)}(E_0) , \tag{44}$$

$$\underline{A}_v(\vec{k}) = \kappa_0\underline{C}_v^{(2)}(E_0) + \underline{B}(E_0, \vec{k})\underline{S}_v^{(2)}(E_0) .$$

Eigenvalues for niobium calculated with QKKR and LKKR equations based on (41)–(44) rather than (31)–(33) are compared with KKR eigenvalues in Fig. 9. The value of E_0 is the same as for Fig. 8, $E_0=0.300$ du, but E_v is chosen to be the energy at which the matrix $\underline{C}^{\Delta}(0.300)$ indicates a scattering resonance in the $l=2$ channel, $E_v=0.648\,84$ du. The eigenvalues, particularly the ones calculated with the QKKR, are almost as good as the ones calculated with the optimum choice $E_0=E_v=0.669\,55$ du.

It can be seen from Figs. 8 and 9 that by carrying out calculations for several values of E_v and choosing only the eigenvalues whose magnitudes are close to each E_v, a set of eigenvalues can be obtained from the LKKR that approach the accu-
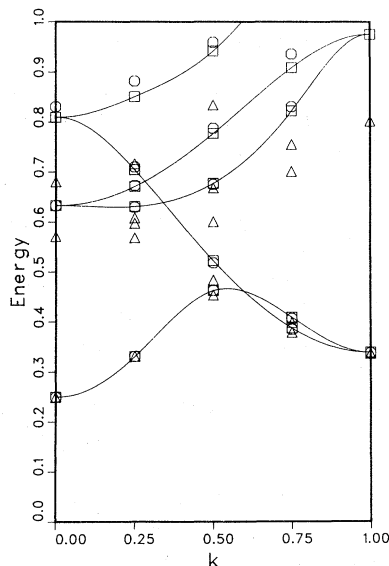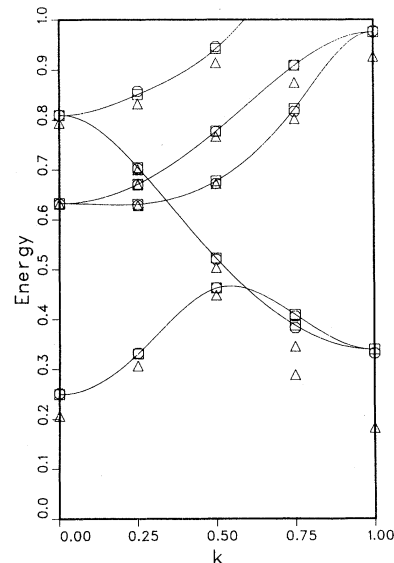

FIG. 8. Quadratic (circles) and linear (triangles) approximation to KKR niobium eigenvalues (squares) calculated with $E_0=0.300$ du.

FIG. 9. Quadratic (circles) and linear (triangles) approximation to the KKR niobium eigenvalues (squares). Modified equations are used with $E_0=0.300$ du and $E_v=0.648\,84$ du.

racy that is achieved in the QKKR. The time re-
quired to find the QKKR eigenvalues for a given
$\vec{k}$ is theoretically about 6 times[10] the amount of
time required for calculating the LKKR eigen-
values because the matrix to be diagonalized is
twice as big. This would appear to indicate that
an LKKR calculation with six values of E_ν would
take no more time than a QKKR calculations.
This argument is not valid because the setting up
of the various matrices to be diagonalized and the
selecting and storing of the subsets of eigenvalues
calculated in such a LKKR takes time. Using
modern methods,[10] the diagonalization of matrices
of the size considered here is a rather trivial com-
putation.

There are, no doubt, many ways to speed up
these calculations. One way that recommends it-
self when iterating a band-theory calculation to
self-consistency is to ignore the contributions from
terms that correspond to angular momenta greater
than $l=2$ in the early stages of the calculation.
Eigenvalues for niobium calculated from QKKR
and LKKR equations that were truncated in this
way are compared with the exact eigenvalues in
Fig. 10. It can be seen that the eigenvalues from
the QKKR are quite good for this choice of E_0
and they are obtained by diagonalizing 18×18 ma-
trices rather than the 50×50 matrices used to get
the eigenvalues in Fig. 5. After this $l_{max}=2$ calcu-
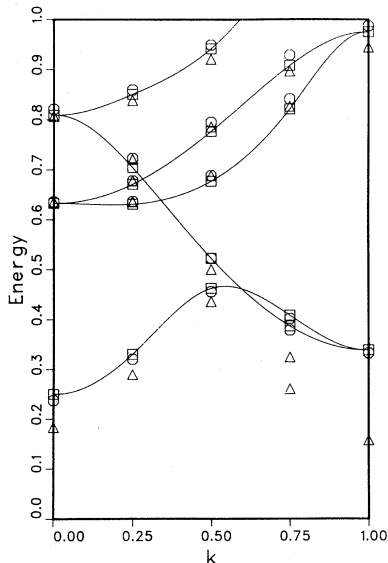lation has been iterated to self-consistency the

FIG. 10. Quadratic (circles) and linear (triangles) ap-
proximations with $l_{max}=2$ and $E_0=0.66955$ du. Exact
KKR eigenvalues calculated with $l_{max}=4$ by squares
and lines.

terms corresponding to l equal to three and four
could be added.

IV. SUMMARY

The discussion in the preceding sections focused
on the calculation of eigenvalues, because the com-
parison with exact eigenvalues is the easiest test for
the accuracy of an approximation. According to
this test, the KKR equations can be replaced by
the QKKR equations with very little loss of accu-
racy. In self-consistent band-theory calculations
and in total-energy calculations, the charge density
$\rho(\vec{r})$ must also be obtained. Using (20) it can be
seen that

$$\rho(\vec{r})=\sum_{\alpha,\vec{k}}{}'\sum_{LL'}\phi_L^{\Delta_\alpha(\vec{k})}(E_0,\vec{r})F_{LL'}^\alpha(\vec{k})\phi_{L'}^{\Delta_{\alpha'}(\vec{k})}(E_0,\vec{r}) ,$$

(45)

where

$$F_{LL'}^\alpha(\vec{k})=C^\alpha(\vec{k})\hat{d}_L^\alpha(\vec{k})\hat{d}_{L'}^\alpha(\vec{k}) .$$

(46)

The first sum in (45) is over all $\vec{k}$ in the unit cell,
but only those α for each $\vec{k}$ that correspond to
occupied states $[E_\alpha(\vec{k})\leq E_F)$. The normalization
constant $C^\alpha(\vec{k})$ is given by

$$C^\alpha(\vec{k})=\left[\sum_{LL'}\hat{d}_L^\alpha(\vec{k})K_{LL'}^{\Delta_\alpha(\vec{k})}\hat{d}_{L'}^\alpha(k)\right]^{-1} ,$$

(47)

where $K_{LL'}^\Delta$ is the integral over the unit cell

$$K_{LL'}^\Delta=\int\phi_L^\Delta(E_0,\vec{r})\phi_{L'}^\Delta(E_0,\vec{r})\,dv .$$

(48)

The matrix elements $K_{LL'}^\Delta$ can be expanded as
polynomials in Δ, just like the elements of the
cosine and sine matrices. It is thus reasonable to
calculate them for a few values of Δ and then in-
terpolate to get the $K_{LL'}^{\Delta_\alpha(\vec{k})}$ that appear in (46). Us-
ing an expression for the Green's function that was
derived in a previous publication[11] and the fact
that the eigenvalues and coefficients in the QKKR
are obtained by a matrix diagonalization, an alter-
native expression for the $F_{LL'}^\alpha(\vec{k})$ has been derived.
The advantage of this alternative expression is that
it does not require the evaluation of any integrals
at all.

It should be emphasized that the reason for us-
ing a muffin-tin potential in these calculations is
so that comparisons can be made with exact KKR
calculations. The term $\Delta\sigma(\vec{r})$ in (19) is not spheri-
cally symmetric, and its magnitude can be much
greater than any nonspherical contribution to $v(\vec{r})$

that would come from a nonspherical charge densi-
ty. Since the off-diagonal elements of the scatter-
ing matrices must be calculated from (27) in any
case, the use of a non-muffin-tin $v(\vec{r})$ causes no
difficulties. It is also interesting to note that the
smooth variation of $\underline{C}^{\Delta}(E_0)$ and $\underline{S}^{\Delta}(E_0)$ with Δ
follows from their definition in (27). The scatter-
ing matrix $\underline{X}^{\Delta}(E_0)$ and the secular matrix
$\underline{P}^{\Delta}(E_0,\vec{k})$ would not be changed significantly if the
sine and cosine matrices were replaced with new
matrices obtained by the transformations,

$$\hat{\underline{C}}^{\Delta}(E_0)=\underline{C}^{\Delta}(E_0)\underline{A}^{\Delta} \ ,$$
$$\hat{\underline{S}}^{\Delta}(E_0)=\underline{S}^{\Delta}(E_0)\underline{A}^{\Delta} \ , \tag{49}$$

where $\underline{A}^{\Delta}$ is an arbitrary function of Δ. There
would clearly be many ways to choose $\underline{A}^{\Delta}$ that

would make the series expansion of the $\underline{c}^{\Delta}(E_0)$ and
$\underline{S}^{\Delta}(E_0)$ less good. An example of such a choice
would be the requirement, for a spherical model,
that the sum of the squares of the sines and con-
sines for a given l should be equal to one.

The QKKR equations developed in this paper
are presently being used in self-consistent total-
energy calculation on transition metals.

ACKNOWLEDGMENTS

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