Accurate evaluation of the interstitial KKR Green function

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It is shown that the Brillouin zone integral for the interstitial KKR Green function can be evaluated accurately by taking proper care of the free-electron singularities in the integrand. The proposed method combines two recently developed methods, a supermatrix method and a subtraction method. This combination appears to provide a major improvement compared with an earlier proposal based on the subtraction method only. Consequently, the barrier preventing the study of important interstitial-like defects, such as an electromigrating atom halfway along its jump path, can be considered as being razed. [S0163-1829(96)07228-1]

I. INTRODUCTION

The Korringa-Kohn-Rostoker (KKR) Green function method[1–3] has proven to be a powerful and elegant approach to calculate the electronic structure of defects in metals.[4] The expressions to be evaluated are exact results of multiple scattering theory and the method has been applied successfully in calculating effects of charge transfer and lattice distortion, both on the electronic structure[4,5] and on physical quantities such as the Dingle temperature[6] and the effective valency of migrating atoms.[7] Until recently its elegance was believed[8,9] to arise only after applying the muffin-tin approximation to the atomic potentials. This amounts to an exact description of the electronic structure within nonoverlapping spheres only, being embedded in an average constant potential, called the muffin-tin zero. Fortunately it could be proven[10–12] that the muffin-tin approximation is not necessary, opening the possibility to do full-potential calculations in the framework of multiple scattering theory as well.

There remains one drawback of multiple scattering theory, and this will be the subject of the present paper. The muffin-tin zero or free-space reference system still appears in the expressions to be evaluated, since free-electron poles are present in the integrand of the KKR Green functions. These plaguing singularities have to be handled with care. As far as substitutional defects are concerned this problem was solved recently[13,14] by implementing a supermatrix method. However, for interstitial defects, such as hydrogen in metals and an electromigrating atom halfway along its jump path, the problem has not yet been solved to our knowledge. In this paper we want to present a solution. It appears that the supermatrix method formulated for substitutional defects can be extended to the interstitial problem. Supplemented with a subtraction method the expressions become manageable and evaluable to a high degree of accuracy.

The paper is organized as follows. In Sec. II the KKR

Green function matrices of interest are defined and the different existing computational approaches are reviewed briefly. In Sec. III the supermatrix method will be presented. In Sec. IV the subtraction procedure will be described. In Sec. V the subtraction method will be tested. The paper ends with some conclusions and prospects.

II. RELEVANT MATRICES AND DIFFERENT APPROACHES

In a calculation of the electronic structure of dilute alloys by use of the KKR Green function technique two matrices show up,[15] one for defects at substitutional sites,

$$T^{jj'} = \frac{1}{\Omega_{BZ}} \int_{BZ} d^3 k e^{i\mathbf{k}\cdot\mathbf{R}_{jj'}} M^{-1}(\mathbf{k}) \qquad (1)$$

and one for an interstitial defect,

$$\mathcal{G}^{pp'} = \frac{1}{\Omega_{BZ}} \int_{BZ} d^3 k e^{i\mathbf{k}\cdot\mathbf{R}_{pp'}} b^p(\mathbf{k}) M^{-1}(\mathbf{k}) b^{p'T}(-\mathbf{k}). \qquad (2)$$

The integrals run over the Brillouin zone (BZ) with volume Ω_{BZ}. A lattice vector $\mathbf{R}_j$ is denoted by a label j and $\mathbf{R}_{jj'}$ stands for the difference vector between the sites j and j'. Arbitrary sites, including nonlattice sites, are indicated by a label p. All matrices are a function of the energy E and carry (suppressed) angular momentum labels L, which stands for (lm). Both integrands contain the inverse of the KKR matrix $M(\mathbf{k})$ given by

$$M(\mathbf{k}) = t^{-1} - b(\mathbf{k}), \qquad (3)$$

in which the matrix t expresses the scattering properties of a host atom, and for spherical scatterers is equal to $-\sin\delta e^{i\delta}$,

δ being scattering phase shifts to be labeled by the angular momentum label l. The matrix $b(\mathbf{k})$ follows from the matrix $b^p(\mathbf{k})$, defined by

$$b^p(\mathbf{k}) = \sum_j B^{pj} e^{-i\mathbf{k}\cdot\mathbf{R}_{pj}}, \tag{4}$$

after taking for p a lattice site label. The matrix $b^p(\mathbf{k})$ is the Fourier transform of the free space propagation matrix element B^{pj}, given by

$$B_{LL'}^{pj} = 4\pi i^{l-l'-1} \sum_{L''} i^{l''} C_{LL'L''} h_{L''}^+(\mathbf{R}_{pj}), \tag{5}$$

in which $C_{LL'L''}$ are Gaunt coefficients and $h_L^+(\mathbf{r}) = h_l^+(\kappa r) Y_L(\hat{r})$. Real spherical harmonics $Y_L(\hat{r})$ are used, h_l^+ are spherical Hankel functions, and $\kappa = \sqrt{E}$. The electronic structure of the metallic host follows from the condition

$$\det M(\mathbf{k}) = 0, \tag{6}$$

which is a basic result of multiple scattering theory.

The free-electron singularities are hidden in the matrix $b^p(\mathbf{k})$. They are readily made explicit by writing down its reciprocal space representation

$$b_{LL'}^p(\mathbf{k}) = \sum_n e^{i\mathbf{K}_n\cdot\mathbf{R}_{pj}} \frac{F_L(\mathbf{k}+\mathbf{K}_n) F_{L'}^*(\mathbf{k}+\mathbf{K}_n)}{(\mathbf{k}+\mathbf{K}_n)^2 - E^+}$$
$$+ i\delta_{pj}\delta_{LL'} \frac{h_l^+(\kappa x)}{j_l(\kappa x)}, \tag{7}$$

in which

$$F_L(\mathbf{k}) = \sqrt{\frac{2\Omega_{\text{BZ}}}{\pi\kappa}} i^l Y_L(\hat{k}) \frac{j_l(kx)}{j_l(\kappa x)}. \tag{8}$$

In this expression the free-electron poles at the energies $E = (\mathbf{k}+\mathbf{K}_n)^2$ are clearly present, $\mathbf{K}_n$ denoting a reciprocal lattice vector. The latter equality in fact defines the so-called free-electron sphere. Note that for p being a lattice site the exponential factor reduces to unity and that only for that case does the second term contribute. The j_l are spherical Bessel functions. As usual in Green function treatments, the energy carries an infinitesimally positive imaginary part, which is indicated by E^+. At this point we want to remark that the formalism discussed in this paper is currently[4] applied at complex energies as well. For that slight changes in the notation are required. However, in all calculations one has to approach the real-energy axis somewhere, so that the pole problem shows up anyhow. It is clear that the matrix $M(\mathbf{k})$ also contains the free-electron singularities. At the $\mathbf{k}$ points defined by Eq. (6), which pertain to the electronic structure, its determinant value is zero, while at the free-electron sphere it is singular.

Looking at the integrand of the matrix $\mathcal{G}^{pp'}$ it is seen that it is full of singularities. Free-electron singularities are present in the matrices $b^p(\mathbf{k})$ and $b^{p'T}(-\mathbf{k})$. These are partially canceled by those in the matrix $M(\mathbf{k})$, but this matrix itself introduces poles corresponding to the electronic structure of the metal regarding the condition Eq. (6).

In order to state the problem in actual calculations clearly we expand a little upon it. A popular way to evaluate the matrices $\mathcal{T}^{jj'}$ and $\mathcal{G}^{pp'}$ is using a subdivision of the Brillouin zone into microvolumes, cubes, or tetrahedrons, going back to Gilat and Raubenheimer,[16] Jepsen and Andersen,[17] and Lehmann and Taut.[18] The required matrix inversion is performed by using its eigenvalues λ and eigenvectors V,

$$M_{LL'}^{-1} = (V\lambda^{-1}V^\dagger)_{LL'} = \sum_q V_{Lq} \frac{1}{\lambda_q} V_{L'q}^*, \tag{9}$$

as suggested by Lasseter and Soven[19] and elaborated by Coleridge, Molenaar, and Lodder.[20] The matrix $\mathcal{T}^{jj'}$ is the simpler one and therefore has been calculated most intensively. This explains the availability of quite exhaustive studies of substitutional alloys and the relative lack of results for interstitial alloys.[21]

As an introduction we concentrate on the different evaluation methods for $\mathcal{T}^{jj'}$. These methods can be distinguished by tracing the influence of the infinitesimally positive imaginary part added to the energy E. Working out this influence explicitly a real and an imaginary part of the integral in $\mathcal{T}^{jj'}$ come out according to the well-known equality

$$\frac{1}{x^+} = P\frac{1}{x} - \pi i\delta(x) \tag{10}$$

The imaginary δ function part leads to a reduction of the Brillouin zone integral to an integral over a constant energy surface. If one is interested in properties at the Fermi energy E_F that integral runs over the Fermi surface. The tetrahedron grid reduces to a grid of triangles over the constant energy surface. The real principal value part remains. In practice it is evaluated along two different lines. The most straightforward line is to evaluate the corresponding Brillouin zone integral explicitly. This is achievable if one needs $\mathcal{T}^{jj'}$ at the Fermi energy only, because quite a fine grid of $\mathbf{k}$ points is required. Coleridge, Molenaar, and Lodder.[20] proposed to use a weighted grid, having a finer subdivision of tetrahedra at the singular surfaces, the Fermi surface, and the free-electron sphere, and that is the way it is applied.[22] For electronic structure calculations one needs the matrix $\mathcal{T}^{jj'}$ at all energies, starting at the bottom of the band and going upwards. To that end another line of evaluation[23] of the real part has been developed, taking advantage of the necessity to account for a considerable energy interval by employing a Kramers-Kronig relation. This relation expresses the real part of $\mathcal{T}^{jj'}$ in terms of its imaginary part in the form of an integral over the energy. In this way the Brillouin zone integration is avoided at the expense of the necessity to evaluate the imaginary part, the constant-energy surface integral, up to relatively high energies. At the latter point some approximation has to be made, in choosing an upper-bound cutoff energy. It is worthwhile to note that in practice in this method the free-electron problem does not enter in the integrals, neither in the evaluation of the real part, nor in integrating over the constant-energy surface. The integrand of the imaginary part simply is a product of unperturbed metallic-host wavefunction coefficients.[23] The free-electron singularities only

complicate the finding of the metallic bands, using Eq. (6), and the corresponding wave-function coefficients.

A relatively recent development[13,24] is to evaluate the full Brillouin zone integral, substituting $E^+ = E + i\delta$ and using a small value for δ. The grid of $\mathbf{k}$ points to be used is not as fine as required for the principal value part, because E^+ now is a complex number, while a value of $\delta = 0.01E$ is already small enough to meet both the $\delta \to 0$ limit and accuracy requirements.

All this applies as far as the pole structure of $M^{-1}(\mathbf{k})$ is concerned, corresponding to the metallic electronic structure. Now we turn to the singularities in $M(\mathbf{k})$ due to the free-electron poles. These singularities do not look too serious, because $M^{-1}(\mathbf{k})$ approaches zero at these points. This is so indeed, if one follows the so-called double linear method of Coleridge, Molenaar, and Lodder.[20] In that method the full matrix $M^{-1}(\mathbf{k})$ is represented as a ratio of two functions $n(\mathbf{k})$ and $d(\mathbf{k})$, and the integral $I(T)$ over a tetrahedron T is written as

$$I(T) = \int_T d^3k \frac{n(\mathbf{k})}{d(\mathbf{k})} = \sum_{i=1}^4 K_i(d_1,d_2,d_3,d_4)n_i. \quad (11)$$

The third member follows analytically from the second member assuming a linear behavior of the functions $n(\mathbf{k})$ and $d(\mathbf{k})$ inside the tetrahedron. The numbers n_i and d_i are the values at the four vertices. The weights K_i are given by Oppeneer and Lodder.[25] The function $d(\mathbf{k})$ is supposed to be zero at the singularities due to the electronic structure. In practice one takes for $d(\mathbf{k})$ the eigenvalue of $M(\mathbf{k})$, which becomes zero, and by that determines the electronic structure. Denoting this eigenvalue by λ_0, the function $n(\mathbf{k})$ in the numerator is equal to $\lambda_0 \Sigma_q V_{Lq} V_{L'q}^* / \lambda_q$. This holds for the alkali and noble metals. If the Fermi surface is composed of more than one sheet more than one eigenvalue becomes zero, of course at different $\mathbf{k}$ points, and a product of the corresponding eigenvalues is used. However, in this approach the function $n(\mathbf{k})$ is not as linear as one might wish, even if just one eigenvalue becomes zero. In addition to smoothly behaving eigenvalues it contains the eigenvalue representing the free-electron singularity. Since, due to the inverse, $n(\mathbf{k})$ at such points becomes zero the method still works, provided a relatively dense (weighted) grid is used.

In a later development[26,27,13] it was considered to apply Eq. (11) not to the full matrix $M^{-1}(\mathbf{k})$, but to each term separately in the representation (9) instead. The functions $d_q(\mathbf{k})$ in the denominator are the roots λ_q, and $n_q(\mathbf{k}) = V_{Lq} V_{L'q}^*$. It is clear that this cannot work without modification, due to the terms corresponding to the highly nonlinear free-electron roots. The modification requires an innovative handling of the free-electron singularities. It appears that the concept of a supermatrix has to be introduced in the description.[26,13] This supermatrix method, which allows for a considerable reduction of the number of $\mathbf{k}$ points to be used,[14] will be discussed in Sec. III.

III. SUPERMATRIX DECOMPOSITION OF THE INTEGRANDS

For the sake of clarity first the formulation for the matrix $\mathcal{T}^{jj'}$ will be summarized,[13,14] after which it is given for the matrix $\mathcal{G}^{pp'}$. In the supermatrix method the terms in the matrix $b(\mathbf{k})$, which make the matrix $M(\mathbf{k})$ singular, are treated separately in a special way. Suppose that a total number of N reciprocal lattice vectors contribute to the singularity in the energy range of interest. Then, glancing at Eqs. (3) and (7), it is possible to write the matrix $M(\mathbf{k})$ as a sum of a smooth part $M^0(\mathbf{k})$ and a part containing the N possible singularities as follows:

$$M_{LL'}(\mathbf{k}) = M_{LL'}^0(\mathbf{k}) - \sum_n^N \frac{F_L(\mathbf{k}+\mathbf{K}_n)F_{L'}^*(\mathbf{k}+\mathbf{K}_n)}{(\mathbf{k}+\mathbf{K}_n)^2 - E^+}. \quad (12)$$

After defining a square diagonal matrix D with elements $D_n = (\mathbf{k}+\mathbf{K}_n)^2 - E^+$ and a rectangular matrix F with elements $F_{Ln} \equiv F_L(\mathbf{k}+\mathbf{K}_n)$, this equation can be written in matrix form as

$$M = M^0 - FD^{-1}F^\dagger. \quad (13)$$

This form suggests inversion using a supermatrix A defined by

$$A = \begin{bmatrix} D & F^\dagger \\ F & M^0 \end{bmatrix} \quad (14)$$

according to the Sherman-Morrison-Woodbury formula[28]

$$A^{-1} = \begin{bmatrix} D^{-1} + D^{-1}F^\dagger M^{-1}FD^{-1} & -D^{-1}F^\dagger M^{-1} \\ -M^{-1}FD^{-1} & M^{-1} \end{bmatrix}. \quad (15)$$

Contrary to the original matrix M, the supermatrix A is regular everywhere in the Brillouin zone. The free-electron poles in M appear in its supermatrix representation A as free electron zeros of the matrix D in the upper left corner of A. It is even so that $\det A = \det D \det M$, which is clear from the following equality

$$\det A = \det \begin{bmatrix} D & F^\dagger \\ F & M^0 \end{bmatrix} = \det\left(\begin{bmatrix} 1 & 0 \\ FD^{-1} & 1 \end{bmatrix}\right.$$
$$\left. \times \begin{bmatrix} D & F^\dagger \\ 0 & M^0 - FD^{-1}F^\dagger \end{bmatrix}\right) = \det 1 \det 1 \det D \det M,$$
$$(16)$$

by using Eq. (13). One simple consequence is that the unpleasant original KKR condition Eq. (6) can be replaced by the regular one

$$\det A(\mathbf{k}) = 0. \quad (17)$$

This difference between A and M is crucial regarding the accuracy of the integration. According to Eq. (15) the wanted inverted matrix M^{-1} is given simply by the lower right block of the supermatrix A^{-1}. In the inversion of A, to be achieved in a way similar to Eq. (9), using its eigenvalues and eigenvectors, all eigenvalues behave smoothly. Applying the double linear method symbolized by Eq. (11) to each term separately in the sum over the inverse eigenvalues, a mesh of about 100 $\mathbf{k}$ points is sufficient in most self-consistent electronic-structure calculations. The eigenvector products $n_q(\mathbf{k})$ in the numerator even behave so smoothly

that it appears to be sufficient to use the value of the functions $n_q(\mathbf{k})$ in the middle points of the tetrahedron only. By that the third member of Eq. (11) becomes proportional to that value, while the sum over the weights K_i reduces to one simple weight expression. A convincing example of the power of the supermatrix method is given in Ref. 14.

Now everything is ready to focus our attention on the much more singular integrand of the interstitial KKR Green function matrix $\mathcal{G}^{pp'}$. Fortunately a similar decomposition of that integrand can be designed. In addition to the form (13) for the matrix M one needs the forms

$$b^p(\mathbf{k}) = b^{l0} + F^p D^{-1} F^\dagger \qquad (18)$$

and

$$b^{pT}(-\mathbf{k}) = b^{r0} + F D^{-1} F^{p\dagger} \qquad (19)$$

for the two b matrices in the integrand in Eq. (2). The matrix F^p is defined by

$$F_{Ln}^p = e^{i\mathbf{K}_n \cdot \mathbf{R}_p} F_{Ln}. \qquad (20)$$

Using the form (15) for the supermatrix A^{-1} it is readily seen that the supermatrix P, defined by the product of three supermatrices,

$$P = \begin{bmatrix} D & F^\dagger \\ 0 & b^{l0} + F^p D^{-1} F^\dagger \end{bmatrix}$$
$$\times \begin{bmatrix} D & F^\dagger \\ F & M^0 \end{bmatrix}^{-1} \begin{bmatrix} D & 0 \\ F & b^{r0} + F D^{-1} F^{p'\dagger} \end{bmatrix}, \qquad (21)$$

after multiplication gets a lower right block, which is precisely the matrix product in the integrand of Eq. (2). The left and right supermatrices in Eq. (21) do not behave smoothly yet, but after some rewritings, to be given in Appendix I, the supermatrix P obtains the form

$$P = \begin{bmatrix} D & 0 \\ 0 & -F^p D^{-1} F^{p'\dagger} \end{bmatrix} + \begin{bmatrix} 0 & 0 \\ -F^p & b^{l0} \end{bmatrix}$$
$$\times \begin{bmatrix} D & F^\dagger \\ F & M^0 \end{bmatrix}^{-1} \begin{bmatrix} 0 & -F^{p'\dagger} \\ 0 & b^{r0} \end{bmatrix}. \qquad (22)$$

The second term contains the inverse of the supermatrix A, now multiplied from the left and right by a smooth matrix. Since A^{-1} can be obtained in a smooth way, the second term is easily evaluable. Only the free-electron poles in the lower right block of the first term still require special treatment. It can be shown that a subtraction procedure presented recently[14] allows for a quick and accurate evaluation of that term as well. This will be the subject of the next section.

IV. THE SUBTRACTION IDEA

Originally[14] the subtraction method was designed and applied in handling the free-electron singularities in the integrand of the matrix $\mathcal{G}^{pp'}$ according to Coleridge, Molenaar, and Lodder,[20] using a weighted distribution of tetrahedra in the Brillouin zone. For the sake of clarity that approach will be summarized first.

The idea of the subtraction method is to subtract a function $f(\mathbf{k})$ from the integrand, which is chosen such that the integrand gets free of the poles, while the integral over the function $f(\mathbf{k})$ can be evaluated analytically and is added later on. Although it can be seen by inspecting the behavior of the integrand of Eq. (2) at the free-electron poles that the function

$$-\sum_n e^{i(\mathbf{k}+\mathbf{K}_n)\cdot\mathbf{R}_{pp'}} \frac{F_L(\mathbf{k}+\mathbf{K}_n) F_{L'}^*(\mathbf{k}+\mathbf{K}_n)}{(\mathbf{k}+\mathbf{K}_n)^2 - E^+} \qquad (23)$$

cancels these poles in the integrand, an explicit proof will be given in Appendix B. This function cannot be integrated analytically. However, it is possible to manipulate the form (23) such that it retains its pole-canceling property on the one hand and can be integrated on the other hand. First the functions $F_L(\mathbf{k})$ given by Eq. (8) can be used in a simplified form by taking the limit $k \rightarrow \kappa$, by which the Bessel function factor reduces to unity. This step may induce some oscillations around the free-electron singularities, but at the singularity the limit holds exactly. Another step is the introduction of an Ewald-like convergence factor in order to improve the convergence of the summation over reciprocal lattice vectors. The final function $f(\mathbf{k})$ obtains the form

$$f_{LL'}(\mathbf{k}) = -\frac{2\Omega_{\text{BZ}}}{\pi\kappa} i^{l-l'} \sum_n e^{i(\mathbf{k}+\mathbf{K}_n)\cdot\mathbf{R}_{pp'}} \frac{Y_L(\mathbf{k}+\mathbf{K}_n) Y_{L'}(\mathbf{k}+\mathbf{K}_n)}{(\mathbf{k}+\mathbf{K}_n)^2 - E^+} e^{-(|\mathbf{k}+\mathbf{K}_n|-\kappa)^2/\eta}, \qquad (24)$$

in which the Ewald parameter η controls the convergence. Upon integration over the Brillouin zone, the summation over reciprocal lattice vectors leads to an integral over all $\mathbf{k}$ space. The angular part of the resulting integral can be carried out

$$\int d\hat{k} e^{i\mathbf{k}\cdot\mathbf{R}_{pp'}} Y_L(\hat{k}) Y_{L'}(\hat{k}) = 4\pi \sum_{L''} i^{l''} C_{LL'L''} j_{l''}(kR_{pp'}) Y_{L''}(\hat{R}_{pp'}). \qquad (25)$$

The integral over k still contains a free-electron pole, but the principal value part can be evaluated using the equality

$$\mathrm{P}\int_0^\infty k^2 dk \frac{j_l(kR_{pp'})e^{-(k-\kappa)^2/\eta}}{k^2-E} = \mathrm{P}\int_0^\infty dk\left(\frac{k^2 j_l(kR_{pp'})}{k+\kappa} - \frac{\kappa}{2}j_l(\kappa R_{pp'})\right)\frac{e^{-(k-\kappa)^2/\eta}}{k-\kappa} + \frac{\kappa}{4}j_l(\kappa R_{pp'})\mathrm{P}\int_0^\infty 2dk\frac{e^{-(k-\kappa)^2/\eta}}{k-\kappa}.$$

(26)

The first integral on the right-hand side is regular, while the second integral equals the readily available exponential integral $E_1(E/\eta)$, being defined by[29]

$$E_1(x) = \int_x^\infty \frac{e^{-t}}{t}dt. \tag{27}$$

In this way the evaluation of the matrix $\mathcal{G}^{pp'}$ connecting two nonlattice sites $\mathbf{R}_p$ and $\mathbf{R}_{p'}$ has been made possible, although it has to be admitted that in the used weighted mesh sometimes over 4000 $\mathbf{k}$ points are required.

Now we return to the supermatrix P, Eq. (22). From Eq. (20) one readily sees that the matrix $F^p D^{-1}F^{p'\dagger}$ in the lower right block of the supermatrix in the right-hand side of Eq. (22) has precisely the form (23). Note that in Eq. (23) the exponential factor $e^{i\mathbf{k}\cdot\mathbf{R}_{pp'}}$ in the integrand of $\mathcal{G}^{pp'}$, Eq. (2), has already been included, while the lower right block of P represents the matrix product in Eq. (2) only. So the only real difference between the matrix function $-F^p D^{-1}F^{p'\dagger}$ and Eq. (23) pertains to the summation over reciprocal lattice vectors. In Eq. (23) all of them are included, while in P only the N pole-generating ones occur. From above it is clear that the function $f(\mathbf{k})$ of Eq. (24) has the same properties as Eq. (23) as far as the free-electron poles are concerned. It can be concluded that precisely that function can serve in evaluating the remaining problematic Brillouin zone integral. The function $-F^p D^{-1}F^{p'\dagger}$ can be calculated straightforwardly, and after subtraction of $f(\mathbf{k})$ given by Eq. (24) it becomes smooth.

By this the barrier in evaluating the interstitial KKR Green function $\mathcal{G}^{pp'}$ can be considered as being razed. In addition, the achievement of the supermatrix approach, in that a coarser mesh suffices compared with the original Coleridge approach, remains. The subtraction method will be tested below.

V. TEST CALCULATIONS

In this section the accuracy of two integrals will be tested, both of which suffer from the presence of free-electron singularities in the integrand. The integrations will be carried out using the Coleridge approach[20] symbolized by Eq. (11). The first integral is given by the left-hand side of the following algebraic equality:

$$\frac{1}{\Omega_{\mathrm{BZ}}}\int_{\mathrm{BZ}} b_{LL'}(\mathbf{k})e^{i\mathbf{k}\cdot\mathbf{R}_{jj'}}d^3k = B_{LL'}^{jj'}. \tag{28}$$

The B matrix in the right-hand side, for different site labels defined by Eq. (5), is evaluated routinely up to any desired accuracy. If $j'=j$ this matrix is defined to be zero, in accordance with the exact result for the integral on the left-hand side. The b matrix in the integrand, being given by the ma-

trix b^p of Eq. (4) for $p=j$, is seen to be singular on the free-electron sphere by inspecting the alternative representation, Eq. (7). Comparing with the matrix function $F^p D^{-1}F^{p'\dagger}$ in Eq. (22), clearly the singular part of the matrix b coincides with it if p and p' refer to lattice sites labeled by j and j'. So the integral of the b matrix can be considered as a close test of the subtraction procedure proposed. Furthermore, the choice is quite natural, because this matrix is readily available in our computer codes.

The actual tests have been done for copper at the Fermi energy. Using a muffin-tin radius of $0.65a/2$ and a lattice constant a of 6.831 bohrs, the phase shifts δ_0 to δ_3 are -0.1506388, 0.0563578, -0.1491734, and 0.0010149, respectively, and $E_F=0.634$ Ry. In the first test only the lattice constant and the Fermi energy enter.

In Table I results obtained without and with subtraction are compared with the exact results according to the right-hand side of Eq. (28). Only some representative matrix elements are shown, indicated by (jlm) labels in the first six columns. The seventh to tenth columns are obtained by numerical integration, the last column gives the exact values. The first row at the top indicates the way in which the integration is performed, and the second and third rows specify the mesh and the denominator function $d(\mathbf{k})$ in Eq. (11), respectively. So, the seventh column follows from straight integration. Application of subtraction of the function $f(\mathbf{k})$, defined in Eq. (24), is indicated explicitly. As for the second row at the top, straightforward integration requires a weighted mesh, which, in the present example, is denser near the free-electron sphere, and therefore is indicated by FES. After subtraction the smooth integrand allows for a homogeneous grid, indicated by 0. Nevertheless the smoothness is tested by doing the same calculation with the weighted grid. The number of $\mathbf{k}$ points is given in the last row of the table. The singular surface is the free-electron sphere and the denominator function $d(\mathbf{k})$ required for the straightforward integration is a product of factors $(\mathbf{k}+\mathbf{K}_n)^2-E$, as many of them that vanish somewhere in the Brillouin zone. Interestingly, this latter product is precisely equal to $\det D$, the determinant value of the matrix D in the upper left block of the supermatrix A, introduced in Eq. (14). This is indicated in the third row at the top. After subtraction $d(\mathbf{k})$ can be chosen freely, and a constant, indicated by 1, is used. As an implicit test of the linearity of $\det D$, also after subtraction a calculation is done using that function as a denominator, given in the tenth column. Of course, in that case the weighted mesh FES is required again. Comparing the seventh and eighth columns with the last column it is seen that application of subtraction leads to a major improvement. Furthermore, the better result is obtained with a much coarser mesh. Applying the finer mesh after subtraction, as shown in the ninth column, does not lead to significant changes. In addition it can be concluded from the tenth column that the linearity of $\det D$ is sufficient.

TABLE I. $B_{LL'}^{jj'}$ calculated by integration of $b(\mathbf{k})$ in different ways. The last column contains its exact value.

		$B_{LL'}^{jj'}$ labels				Straight	$f(\mathbf{k})$	$f(\mathbf{k})$	$f(\mathbf{k})$	Exact
						FES	0	FES	FES	
j	j'	l	m	l'	m'	det$D$	1	1	det$D$	
1	1	0	0	0	0	0.023	0.000	0.000	0.001	0
		1	0	1	0	0.023	0.000	0.000	0.001	0
		2	1	2	1	0.¬049	0.001	0.000	0.003	0
		3	2	3	2	0.223	0.017	0.006	0.139	0
		1	0	3	0	0.040	0.000	0.000	-0.002	0
2	1	0	0	0	0	0.207	0.199	0.199	0.205	0.198
		1	0	1	0	0.164	0.172	0.172	0.178	0.172
		2	1	2	1	0.464	0.470	0.470	0.477	0.469
		3	2	3	2	2.794	2.649	2.647	2.709	2.629
		1	0	3	0	0.457	0.456	0.455	0.457	0.455
Number of $\mathbf{k}$ points						2247	640	2247	2247	

Another test can be derived from the matrix $\mathcal{G}^{pp'}$ [see Eq. (2)] if the arbitrary site labels are replaced by lattice site labels. Then, because $b^j(\mathbf{k}) = b^{j'T}(-\mathbf{k}) = b(\mathbf{k})$, the algebraic identity

$$\mathcal{G}^{jj'} = -t^{-1}\delta_{jj'} - B^{jj'} + t^{-1}\mathcal{T}^{jj'}t^{-1} \qquad (29)$$

can be derived easily, using the relation (3) between $M(\mathbf{k})$ and $b(\mathbf{k})$. Both matrices $\mathcal{G}$ and $\mathcal{T}$ can be evaluated numerically only. However, while the integrand of $\mathcal{G}^{jj'}$ contains free-electron singularities, in the integrand of $\mathcal{T}^{jj'}$ they merely appear as a nonlinearity in the eigenvalues of the matrix $M(\mathbf{k})$, as described in Sec. II. In the tests $\mathcal{G}^{jj'}$ is evaluated only according to the original Coleridge approach,[20] including a subtraction procedure as well, in the way the present authors have described recently.[14] The matrix $\mathcal{T}^{jj'}$ will be calculated by the supermatrix method also, for which fewer $\mathbf{k}$ points are expected to be required. So features of both the subtraction and supermatrix methods will be illustrated by Eq. (29).

In Table II results for $\mathcal{G}^{jj'}$ according to the left-hand side of Eq. (29), before and after applying the subtraction procedure, are compared with results according to the right-hand side. This table is constructed in the same way as Table I. First we elucidate the denominator functions $d(\mathbf{k})$ of Eq. (11), as specified in the third row at the top. As far as the poles corresponding to the electronic structure are concerned, the product of the vanishing eigenvalues of $M(\mathbf{k})$ can be taken, as described in Sec. II. Det$M(\mathbf{k})$ might work as well, being equal to the product of *all* eigenvalues. But the latter choice introduces a problem because of its singular (and therefore nonlinear) behavior at the free-electron surface. Therefore, det$M(\mathbf{k})$ has to be multiplied by det$D$. By that additional multiplication, regarding Eq. (16), the denominator function $d(\mathbf{k})$ becomes equal to det$A$, which appears in the modified KKR condition Eq. (17). The free-electron singularities in the integrand of $\mathcal{G}^{jj'}$ require multiplication by an additional factor of det$D$. So for straightforward integration (see column 7) det$A$det$D$ has to be used. In that case the (weighted) mesh must be taken to be dense near both the

Fermi surface and the free-electron sphere. This mesh is indicated by FS/FES. After subtraction the free-electron singular surface is absent. This allows for the less dense mesh FS and for the simpler denominator function det$A$, column 8. To see the influence of the density of the mesh the same calculation is done with the denser FS/FES mesh, column 9. In addition, also in this complicated case, the effect of the (extra) nonlinearity of the denominator is investigated, by doing the same calculation with the denominator det$A$det$D$, as shown in column 10. Columns 11 to 13 give results according to the right-hand side of Eq. (29), the last two columns showing supermatrix results for two different meshes. Contrary to the weighted meshes of the Coleridge method, the meshes used in the supermatrix method are always uniform.

Again the results improve largely by applying subtraction. In fact, the straightforwardly evaluated integrals can be considered as really bad. An obvious source of inaccuracy is the behavior of the denominator function det$A$det$D$ in regions where a tetrahedron is cut by the Fermi surface as well as the free-electron sphere. Then the product of det$A$ and det$D$ does not change sign and the denominator does not become aware of crossing a singular surface at all. This may happen even for a noble metal. The single sheet Fermi surface intersects the free-electron sphere in the neck region. Comparing columns 8 and 9 one sees that the denser mesh near the free-electron surface yields not too large but yet non-negligible modifications. The addition of the extra factor det$D$ is not as harmless as in the integration of $b(\mathbf{k})$, as can be seen from column 10. This is just another illustration of the source of inaccuracy indicated above. So it can be stated that it is important to use a denser mesh at the free-electron sphere, even if the integrand is not singular there. This certainly is a disadvantage of the Coleridge method. Nevertheless, it is satisfactory to see (columns 11 to 13) that, in evaluating the $\mathcal{T}$ matrix, the Coleridge method leads to the same results as the supermatrix method. In addition the table confirms explicitly that the subtraction method, proposed recently[14] for determining the full $\mathcal{G}$ matrix, is reliable.

Finally, the table shows implicitly that the supermatrix method for determining the $\mathcal{G}$ matrix is more efficient than the subtraction method.[14] Less than 1000 $\mathbf{k}$ points are suffi-

TABLE II. The matrix $\mathcal{G}_{LL'}^{jj'}$ calculated along different lines. rhs denotes right-hand side.

$\mathcal{G}_{LL'}^{jj'}$ labels						Straight FS/FES $\det A \det D$	$f(\mathbf{k})$ FS $\det A$	$f(\mathbf{k})$ FS/FES $\det A$	$f(\mathbf{k})$ FS/FES $\det A \det D$	rhs FS/FES $\det A$	rhs super matrix	rhs super matrix
j	j'	l	m	l'	m'							
1	1	0	0	0	0	-0.289	-0.153	-0.150	-0.190	-0.149	-0.155	-0.155
		1	0	1	0	0.008	0.166	0.160	0.106	0.161	0.180	0.169
		2	1	2	1	0.351	0.538	0.524	0.461	0.525	0.551	0.536
		3	2	3	2	2.201	2.311	2.366	2.371	2.486	2.278	2.284
		1	0	3	0	0.061	0.105	0.089	0.080	0.087	0.106	0.106
2	1	0	0	0	0	0.014	-0.002	-0.006	-0.001	0.000	-0.006	-0.005
		1	0	1	0	-0.151	-0.139	-0.137	-0.146	-0.132	-0.137	-0.138
		2	1	2	1	-0.026	-0.047	-0.052	-0.054	-0.045	-0.045	-0.042
		3	2	3	2	-0.568	-0.488	-0.522	-0.448	-0.435	-0.595	-0.601
		1	0	3	0	-0.027	-0.079	-0.080	-0.079	-0.077	-0.068	-0.061
Number of $\mathbf{k}$ points						4123	2643	4123	4123	4123	146	891

cient. The number of 891 in the last column is a good indication for integrating the second term in Eq. (22), which contains the same supermatrix A^{-1} as the supermatrix integrand of the matrix $\mathcal{T}$. The subtraction procedure proposed for the first term, having free-electron poles only, is tested by Table I. The number of 640 $\mathbf{k}$ points in the eighth column suffices for that term.

VI. CONCLUSIONS AND PROSPECTS

The supermatrix method, initially proposed[14] with the aim of a fast and accurate evaluation of the KKR Green function $\mathcal{T}^{jj'}$ appearing in calculations of the electronic structure of substitutional alloys, has been extended to the interstitial KKR Green function $\mathcal{G}^{pp'}$. A subtraction procedure is shown to resolve the remaining problem of integrating a function with free-electron singularities only. In evaluating the corresponding Brillouin zone integrals rather coarse grids of less than 1000 $\mathbf{k}$ points can be used. Applications to calculations of transport properties such as the effective valence of electromigrating atoms are in progress.[30] Study of the electronic structure of the largely unexplored interstitial defects will be the subject of future investigations.

APPENDIX A

We want to give a derivation of the final form Eq. (22) of the supermatrix P from its definition Eq. (21). Using the matrix A defined by Eq. (14) we first write the matrix P in a slightly more compact form:

$$P = \begin{bmatrix} D & F^\dagger \\ 0 & b^{l0} + F^p D^{-1} F^\dagger \end{bmatrix} A^{-1} \begin{bmatrix} D & 0 \\ F & b^{r0} + F D^{-1} F^{p'\dagger} \end{bmatrix}. \tag{A1}$$

Subsequently the supermatrix left of the supermatrix A^{-1} is written in the form $X^l A + Y^l$ and the supermatrix to the right is written similarly as $A X^r + Y^r$. In principle, the choice of the four matrices X^l, Y^l, X^r, and Y^r is arbitrary, but a suitable one is

$$X^l = \begin{bmatrix} 1 & 0 \\ F^p D^{-1} & 0 \end{bmatrix}, \qquad Y^l = \begin{bmatrix} 0 & 0 \\ -F^p & b^{l0} \end{bmatrix}, \tag{A2}$$

$$X^r = \begin{bmatrix} 1 & D^{-1} F^{p'\dagger} \\ 0 & 0 \end{bmatrix}, \qquad Y^r = \begin{bmatrix} 0 & -F^{p'\dagger} \\ 0 & b^{r0} \end{bmatrix}. \tag{A3}$$

The elaboration of Eq. (A1) is now straightforward and ends up with the expression

$$P = \begin{bmatrix} D & 0 \\ 0 & -F^p D^{-1} F^{p'\dagger} \end{bmatrix} + \begin{bmatrix} 0 & 0 \\ -F^p & b^{l0} \end{bmatrix} A^{-1} \begin{bmatrix} 0 & -F^{p'\dagger} \\ 0 & b^{r0} \end{bmatrix}. \tag{A4}$$

Regarding the definition of the supermatrix A, Eq. (14), this is precisely the required form Eq. (22) given in the main text.

APPENDIX B

We want to show that the function (23) indeed cancels the free-electron poles in the integrand of the interstitial KKR Green function (2). Apart from the trivial exponential factor $e^{i\mathbf{k}\cdot\mathbf{R}_{pp'}}$, the integrand, being a matrix to be denoted as a, can be written in the following form:

$$a = (b^{l0} + F^p D^{-1} F^\dagger)(M^0 - F D^{-1} F^\dagger)^{-1}(b^{r0} + F D^{-1} F^{p'\dagger}), \tag{B1}$$

in which Eqs. (13), (18), and (19) are used. First we define a matrix c,

$$c=(M^0-FD^{-1}F^\dagger)^{-1}(b^{r0}+FD^{-1}F^{p'\dagger}), \quad \text{(B2)}$$

being equal to the product of two matrices in the triple product matrix a. So

$$a=b^{l0}c+F^pD^{-1}F^\dagger c, \quad \text{(B3)}$$

while Eq. (B2) can be written in the form

$$FD^{-1}F^\dagger c=M^0c-b^{r0}-FD^{-1}F^{p'\dagger}. \quad \text{(B4)}$$

Three observations can be made. First, from its definition it is clear that the matrix c is a regular one, because the poles in numerator and denominator cancel. Secondly, as a consequence, only the second term in Eq. (B3) contains the free-electron poles. Thirdly, the left-hand side of Eq. (B4) already has the form of that second term. Regarding Eq. (20) it becomes equal to that second term by multiplying Eq. (B4) from the left with the factor $e^{i\mathbf{K}_n\cdot\mathbf{R}_p}$. By that the third term on the right-hand side of Eq. (B4) obtains the required form $-F^pD^{-1}F^{p'\dagger}$. Substituting the rewritten form of Eq. (Br) in Eq. (B3) completes a first proof. The merit of the second proof to be given is, that in addition it exhibits a nice link[27] between the subtraction and supermatrix methods.

To that end an auxiliary rectangular matrix q is defined by the relation

$$F^\dagger c=-F^{p'\dagger}-Dq \quad \text{(B5)}$$

by which Eq. (B4) reduces to

$$Fq=-M^0c+b^{r0}. \quad \text{(B6)}$$

Now Eqs. (B5) and (B6) can be combined in a supermatrix form

$$\begin{bmatrix} D & F^\dagger \\ F & M_0 \end{bmatrix}\begin{bmatrix} q \\ c \end{bmatrix}=\begin{bmatrix} -F^{p'\dagger} \\ b^{r0} \end{bmatrix}. \quad \text{(B7)}$$

It is seen that the supermatrix A, Eq. (14), enters the formulation.

The solution of Eq. (B7),

$$\begin{bmatrix} q \\ c \end{bmatrix}=A^{-1}\begin{bmatrix} -F^{p'\dagger} \\ b^{r0} \end{bmatrix}=\begin{bmatrix} A_{11}^{-1} & A_{12}^{-1} \\ A_{21}^{-1} & A_{22}^{-1} \end{bmatrix}\begin{bmatrix} -F^{p'\dagger} \\ b^{r0} \end{bmatrix}, \quad \text{(B8)}$$

requires the subblocks A_{ij}^{-1} of the supermatrix A^{-1}, by definition given by

$$\begin{bmatrix} D & F^\dagger \\ F & M_0 \end{bmatrix}\begin{bmatrix} A_{11}^{-1} & A_{12}^{-1} \\ A_{21}^{-1} & A_{22}^{-1} \end{bmatrix}=\begin{bmatrix} I & 0 \\ 0 & I \end{bmatrix}. \quad \text{(B9)}$$

We only need the two explicitly written equations

$$DA_{11}^{-1}+F^\dagger A_{21}^{-1}=I, \quad DA_{12}^{-1}+F^\dagger A_{22}^{-1}=0. \quad \text{(B10)}$$

After substitution of the matrix c according to Eq. (B8) in Eq. (B3) for the matrix of interest a,

$$a=(b^{l0}+F^pD^{-1}F^\dagger)(-A_{21}^{-1}F^{p'\dagger}+A_{22}^{-1}b^{r0}), \quad \text{(B11)}$$

and making use of the equalities (B10), one finds

$$a=-b^{l0}A_{21}^{-1}F^{p'\dagger}+b^{l0}A_{22}^{-1}b^{r0}+F^pA_{11}^{-1}F^{p'\dagger}-F^pA_{12}^{-1}b^{r0}$$
$$-F^pD^{-1}F^{p'\dagger}, \quad \text{(B12)}$$

in which form once again the term containing the free-electron poles is made explicit.

Up to now the matrix a figures in the subtraction method only, standing for the singular matrix in the integrand of the interstitial KKR Green function matrix $\mathcal{G}^{pp'}$. It is interesting to go one step further and to write Eq. (B12) in the matrix form

$$a=\begin{bmatrix} -F^p & b^{l0} \end{bmatrix}A^{-1}\begin{bmatrix} -F^{p'\dagger} \\ b^{r0} \end{bmatrix}-F^pD^{-1}F^{p'\dagger}. \quad \text{(B13)}$$

In this form one recognizes the lower right block of the supermatrix P, Eq. (A4), which figures in the supermatrix method. So the supermatrix and subtraction procedures appear to be intimately linked.

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