Empty-lattice test for non-muffin-tin multiple-scattering equations

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(Received 17 February 1988; revised manuscript received 18 April 1988)

The extension of the Korringa-Kohn-Rostocker band-theory method to non-muffin-tin potentials is studied analytically for the case of an empty lattice with a constant potential. The magnitude of the potential is used as an expansion parameter and to first order the exact eigenvalues are obtained. Second- and third-order corrections are studied and shown to vanish if the correct form of the multiple-scattering equations is used. It is conjectured that also all higher-order corrections vanish in the empty-lattice case. The errors arising from a truncation in the angular-momentum expansion are investigated numerically, and it is shown that the convergence is much better than previously believed.

I. INTRODUCTION

The multiple-scattering band theory, originally derived by Korringa[1] and by Kohn and Rostoker[2] (KKR) for the case of muffin-tin potentials, plays a central role in electronic-structure calculations, particularly for disordered metallic alloys by the KKR-(CPA) (coherent-potential-approximation) method[3-5] and for impurities in metals by the KKR Green's-function method.[6,7] These calculations heavily rely on the fact that multiple-scattering theory for muffin-tin potentials can be separated into single-scattering properties depending on the single-site potentials and into structural properties not depending on the potentials. It would be very desirable to have this separation also for the case of general non-muffin-tin potentials. This seems to be a difficult problem and several different suggestions have been published in the past as to how the multiple-scattering equations can be extended to the general case.[8-18] Unfortunately, some of the earlier authors,[11-13] who claimed that a separation is possible in the general case, derived their equations with unjustified assumptions. Ziesche[19] and Faulkner[20] have argued that a correct derivation must contain the so-called near-field effects which probably prevent the separation between structure and potential-dependent terms. On the other hand, by presenting new arguments Brown and Ciftan,[21,22] Gonis,[15] and Zeller[17] have recently tried to show that a separation is possible with the same structure dependence for the cases of non-muffin-tin and muffin-tin potentials. However, although these authors agree on that they have derived *exact* multiple-scattering equations showing the separation, they disagree on the analytical form of the multiple-scattering equations and on the situations where they can be applied and where they fail. Therefore it is desirable to investigate a model for which the exact energy eigenvalues are known and to see if and how the different proposals for multiple-scattering equations lead to these eigenvalues. The model always used in such investigations[13,18,21-24] is the empty lattice with a constant potential $v(\mathbf{r})=\lambda$. This potential is clearly of non-muffin-tin form when written as a set of nonoverlapping potentials $v(\mathbf{r})=\lambda\sum_m \Theta_m(\mathbf{r})$. The step function $\Theta_m(\mathbf{r})$ has the value 1 inside the mth unit cell and is zero outside. The eigenvalues for the model are easily obtained from the free-electron eigenvalues by a constant shift

$$E_n(\mathbf{k})=|\mathbf{k}+\mathbf{K}_n|^2+\lambda\ , \tag{1}$$

where $\mathbf{k}$ is the Bloch vector and $\mathbf{K}_n$ is a reciprocal-lattice vector. Only Badralexe and Freeman[18] are able to prove analytically that their equations exactly reproduce the eigenvalues given by (1). For all other types of multiple-scattering equations, particularly for the interesting cases with separation between structure and potential dependence,[11-15,17] only numerical investigations were possible.[13,21-24] The most extensive calculations were recently done by Faulkner,[24] who investigated the two-dimensional square lattice including very high angular momenta up to $l_{\max}=56$. He neglected near-field effects, and for the multiple-scattering equations originally given by Williams and van Morgan[12,13] he showed that *if* eigenvalues are converged with $l_{\max}=56$ then they agree with the exact results. Numerical instabilities prevented him to go beyond $l_{\max}=56$ and to see if all eigenvalues converge to the exact results or not. Therefore his calculations are inconclusive as to whether or not near-field effects exist and how large they are.

The aim of the present paper is to investigate analytically the empty lattice with a constant potential within the general potential KKR formalism and to show that for this special case near-field effects vanish faster than to third order in the strength of the potential. This result and the general arguments of Ref. 17 lead to the conjecture that also no higher-order corrections exist, which means near-field exactly vanish for the empty-lattice model. A necessary condition for the present derivation is that certain restrictions for the unit cells are satisfied and the equations originally proposed by Williams and van Morgan[12,13] must be used, whereas the more recent equations by Brown and Ciftan[14] are only approximately valid. The convergence with $l_{\max}$ critically depends on the particular form used for the secular matrix. It is shown that the convergence is similar to that in the Taylor expansion of e^x, but only if the secular matrix given in

Sec. II is used, whereas it is much slower in the form given, e.g., by Williams and van Morgan,[12,13] Faulkner,[20] and Gonis.[15] The present paper is organized as follows. In Sec. II the general multiple-scattering equations are expanded in orders of the magnitude of the constant potential. It is shown in Sec. III that the first-order terms give the exact result (1) in the limit $l_{\max}\to\infty$. The convergence is studied in Sec. IV and numerical results for the case of the two-dimensional square lattice are given. The importance of the present results for practical applications is discussed in Sec. V. Finally, the Appendix is used for treating the more complicated higher-order terms of the expansion.

II. MULTIPLE-SCATTERING EQUATIONS

The present paper is based on the simple observation that the eigenvalues $E_n(\mathbf{k})$ in (1) depend exactly linearly on the constant potential λ. Compared to the case of an arbitrary potential, this linear dependence considerably simplifies the investigation for the empty-lattice case. In order to show that multiple-scattering equations are exact for this special case, it is not necessary to solve them exactly; it suffices to make an expansion in orders of λ and to show that the first-order terms give the correct result (1) and that all higher-order terms vanish. Section V contains a detailed discussion on the connection between the different forms for multiple-scattering equations. For that reason the expansion is considered here only for the multiple-scattering equations as derived by the present author.[17] They can be written for the special case of a constant potential $v(\mathbf{r})=\lambda\sum_m\Theta_m(\mathbf{r})$ as below in Eqs. (2)–(5). The single-site wave function is given by the integral equation

$$R_L(\mathbf{r},E)=J_L(\mathbf{r},E)+\lambda\int_\tau d\mathbf{r}'g(\mathbf{r}-\mathbf{r}',E)R_L(\mathbf{r}',E)\ , \tag{2}$$

where the integration is over the unit cell with volume τ. $J_L(\mathbf{r},E)$ is the product of the spherical Bessel function $j_l(\kappa r)$ and the real spherical harmonic $Y_{lm}(\mathbf{r}/r)$ with the usual notation $r=|\mathbf{r}|$, $\kappa=\sqrt{E}$, and L combining l and m. The free-space Green's function $g(\mathbf{r}-\mathbf{r}',E)$ is given by

$$g(\mathbf{r}-\mathbf{r}',E)=g(|\mathbf{r}-\mathbf{r}'|,E)=-e^{i\kappa|\mathbf{r}-\mathbf{r}'|}/(4\pi|\mathbf{r}-\mathbf{r}'|)\ . \tag{3}$$

The single-site t matrix is given by

$$t_{LL'}(E)=\lambda\int_\tau d\mathbf{r}\,J_L(\mathbf{r},E)R_{L'}(\mathbf{r},E)\ , \tag{4}$$

and the band-structure eigenvalues $E_n(\mathbf{k})$ are obtained from the zeros of the KKR determinant as solutions of

$$\det\left|\delta_{LL'}-\sum_{L''}g_{LL''}(\mathbf{k},E)t_{L''L'}(E)\right|=0\ . \tag{5}$$

The KKR structure constants

$$g_{LL'}(\mathbf{k},E)=\sum_{m\neq0}\exp(i\mathbf{k}\cdot\mathbf{R}_m)g_{LL'}^{(m)}(E) \tag{6}$$

are the usual ones of the muffin-tin case.[1,2] They have the symmetry property $g_{LL'}^{(m)}(E)=(-1)^{l-l'}g_{L'L}^{(m)}(E)$, are not defined for $m=0$, and are given for $m\neq0$ by

$$g_{LL'}^{(m)}(E)=-4\pi i\kappa\sum_{L''}i^{l-l'+l''}C_{LL'L''}H_{L''}(\mathbf{R}_m,E)\ , \tag{7}$$

with the Gaunt coefficients

$$C_{LL'L''}=\int d\Omega_r\,Y_L(\mathbf{r}/r)Y_{L'}(\mathbf{r}/r)Y_{L''}(\mathbf{r}/r)\ . \tag{8}$$

$H_{L''}(\mathbf{R}_m,E)$ is the product of the spherical Hankel function $h_{l''}^{(1)}(\kappa R_m)$ and the real spherical harmonic $Y_{L''}(\mathbf{R}_m/R_m)$, and $\mathbf{R}_m$ is a real lattice vector with length $R_m=|\mathbf{R}_m|$.

A consistent and convergent expansion for (2), (4), and (5) in orders of λ, not limited by the magnitude of λ, is obtained by applying Fredholm's theory to the linear integral equation (2) and to the infinitely dimensional linear system of algebraic equations for the expansion coefficients $c_L(\mathbf{k},E)$ of the Bloch waves,

$$c_L(\mathbf{k},E)=\sum_{L,'L''}g_{LL''}(\mathbf{k},E)t_{L''L'}(E)c_{L'}(\mathbf{k},E)\ , \tag{9}$$

for which (5) represents the condition that the Fredholm determinant vanishes. Equation (2) is solved as[25]

$$R_L(\mathbf{r},E)=J_L(\mathbf{r},E)+\lambda\int_\tau d\mathbf{r}'\Gamma(\mathbf{r},\mathbf{r}',E,\lambda)J_L(\mathbf{r}',E)\ , \tag{10}$$

and the resolvent kernel

$$\Gamma(\mathbf{r},\mathbf{r}',E,\lambda)=\left[g(\mathbf{r}-\mathbf{r}',E)+\sum_{p\geq1}(-\lambda)^pK_p(\mathbf{r},\mathbf{r}',E)\right]\Big/\left[1+\sum_{p\geq1}(-\lambda)^p\delta_p(E)\right] \tag{11}$$

can be obtained from the recursion formulas

$$K_p(\mathbf{r},\mathbf{r}',E)=\delta_p(E)g(\mathbf{r}-\mathbf{r}',E)-\int_\tau d\mathbf{r}''g(\mathbf{r}-\mathbf{r}'',E)K_{p-1}(\mathbf{r}'',\mathbf{r}',E)\ , \tag{12}$$

$$\delta_p(E)=p^{-1}\int_\tau d\mathbf{r}\,K_{p-1}(\mathbf{r},\mathbf{r},E)\ , \tag{13}$$

starting with $K_0(\mathbf{r},\mathbf{r}',E)=g(\mathbf{r}-\mathbf{r}',E)$. Because $K_0(\mathbf{r},\mathbf{r}',E)$ does not exist for $\mathbf{r}=\mathbf{r}'$, it is necessary to make the usual extension $K_0(\mathbf{r},\mathbf{r},E)=0$ leading to $\delta_1(E)=0$. The determinant in (5) can be expanded as

$$\det\left|\delta_{LL'}-\sum_{L''}g_{LL''}(\mathbf{k},E)t_{L''L'}(E)\right|=1+\sum_{p\geq1}(-1)^p\Delta^{(p)}(\mathbf{k},E)\ . \tag{14}$$

In analogy to (12) and (13), the quantity $\Delta^{(p)}(\mathbf{k},E)$ is given by

$$\Delta^{(p)}(\mathbf{k},E)=p^{-1}\sum_L K_{LL}^{(p-1)}(\mathbf{k},E)\ , \tag{15}$$

with

$$K^{(p)}_{LL'}(\mathbf{k},E)=\Delta^{(p)}(\mathbf{k},E)K^{(0)}_{LL'}(\mathbf{k},E) - \sum_{L''} K^{(0)}_{LL''}(\mathbf{k},E)K^{(p,-1)}_{L''L'}(\mathbf{k},E) , \quad (16)$$

$$K^{(0)}_{LL'}(\mathbf{k},E)=\sum_{L''} g_{LL''}(\mathbf{k},E)t_{L''L'}(E) . \quad (17)$$

It should be noted that the parameter λ which usually appears in Fredholm's theory is set equal to 1 in (9) and in (14)–(17).

III. FIRST-ORDER EXPANSION

The result for the eigenvalues $E_n(\mathbf{k})$ to first order in λ is obtained if $R_L(\mathbf{r},E)$ in (10) is replaced by $J_L(\mathbf{r},E)$ and if the single-site t matrix is evaluated as

$$t_{LL'}(E)=\lambda t^{(1)}_{LL'}(E) , \quad (18)$$

with

$$t^{(1)}_{LL'}(E)=\int_\tau d\mathbf{r}\, J_L(\mathbf{r},E)J_{L'}(\mathbf{r},E) . \quad (19)$$

It follows from (15)–(17) that to first order in λ only $\Delta^{(1)}(\mathbf{k},E)$ contributes in (14) and the resulting condition for the eigenvalues $E_n(\mathbf{k})$ is

$$0=1-\lambda \sum_{L,L'} g_{LL'}(\mathbf{k},E_n(\mathbf{k}))t^{(1)}_{L'L}(E_n(\mathbf{k})) . \quad (20)$$

The use of (6) and (19) leads to

$$0=1-\lambda \sum_{L,L'} \sum_{m\neq 0} \exp(i\mathbf{k}\cdot\mathbf{R}_m)g^{(m)}_{LL'}(E_n(\mathbf{k}))\int_\tau d\mathbf{r}\, J_L(\mathbf{r},E_n(\mathbf{k}))J_{L'}(\mathbf{r},E_n(\mathbf{k}))$$

$$=1+i\lambda\kappa_n(\mathbf{k}) \sum_{m\neq 0} \exp(i\mathbf{k}\cdot\mathbf{R}_m)\int_\tau d\mathbf{r} \sum_L J_L(\mathbf{r},E_n(\mathbf{k}))H_L(\mathbf{r}-\mathbf{R}_m,E_n(\mathbf{k})) , \quad (21)$$

with $\kappa_n(\mathbf{k})=[E_n(\mathbf{k})]^{1/2}$. In (21) the generalized addition theorem[26] for products of Bessel functions and spherical harmonics has been used. It can be written as

$$-i\kappa H_L(\mathbf{r}-\mathbf{R}_m,E)=\sum_{L'} g^{(m)}_{LL'}(E)J_{L'}(\mathbf{r},E) , \quad (22)$$

or, equivalently, by using $Y_L(-\mathbf{r}/r)=(-1)^l Y_L(\mathbf{r}/r)$ and the symmetry properties of $g^{(m)}_{LL'}(E)$ as

$$-i\kappa H_{L'}(\mathbf{r}+\mathbf{R}_m,E)=\sum_L J_L(\mathbf{r},E)g^{(m)}_{LL'}(E) . \quad (23)$$

Equation (22) leads for the special case $l=0$ to

$$g(\mathbf{r}-\mathbf{R}_m,E)=-i\kappa \sum_{L'} J_{L'}(\mathbf{r},E)H_{L'}(\mathbf{R}_m,E) \quad (24)$$

when (6) with $C_{00,L'L''}=(4\pi)^{-1/2}\delta_{L'L''}$ is used and when (3) is written in the form

$$g(\mathbf{r}-\mathbf{R}_m,E)=-(4\pi)^{-1/2}i\kappa H_{00}(\mathbf{r}-\mathbf{R}_m,E) .$$

In (22)–(24) the important condition $r<R_m$ must be satisfied for the convergence of the sums over L and L'. When $\mathbf{R}_m$ in (24) is replaced by $\mathbf{r}-\mathbf{R}_m$ the convergence condition reads $r<|\mathbf{r}-\mathbf{R}_m|$ and (21) can be written as

$$0=1-\lambda \sum_{m\neq 0} \exp(i\mathbf{k}\cdot\mathbf{R}_m)\int_\tau d\mathbf{r}\, g(R_m,E_n(\mathbf{k})) =1-\lambda\tau \sum_{m\neq 0} \exp(i\mathbf{k}\cdot\mathbf{R}_m)g(R_m,E_n(\mathbf{k})) \quad (25)$$

because the integrand loses its dependence on $\mathbf{r}$. The normal definition of the reduced KKR structure constants $D_{lm}(\mathbf{k},E)$, see, e.g., Eq. (A2.22) of Ref. 2, can be used to write (25) further as

$$0=1-(\lambda\tau/\sqrt{4\pi})D_{00}(\mathbf{k},E_n(\mathbf{k}))-i\tau\lambda\kappa_n(\mathbf{k})/4\pi , \quad (26)$$

or, alternatively, as a sum over reciprocal-lattice vectors by using Eq. (A2.9) of Ref. 2,

$$0=1-[\lambda\tau\kappa_n(\mathbf{k})/4\pi]\{i+\cot[\kappa_n(\mathbf{k})s]/\sqrt{4\pi}\}+\lambda[j_0(\kappa_n(\mathbf{k})s)]^{-1}\sum_{n'}[|\mathbf{K}_{n'}+\mathbf{k}|^2-E_n(\mathbf{k})]^{-1}j_0(|\mathbf{K}_{n'}+\mathbf{k}|s) , \quad (27)$$

where s is arbitrary provided that s is smaller than the muffin-tin radius. The ansatz

$$E_n(\mathbf{k})=|\mathbf{K}_n+\mathbf{k}|^2+\lambda\varepsilon_n(\mathbf{k}), \quad \kappa_n(\mathbf{k})=[E_n(\mathbf{k})]^{1/2} \quad (28)$$

leads to

$$0=1-[\lambda\tau\kappa_n(\mathbf{k})/4\pi]\{i+\cot[\kappa_n(\mathbf{k})s]/\sqrt{4\pi}\}-[\varepsilon_n(\mathbf{k})j_0(\kappa_n(\mathbf{k})s)]^{-1}j_0(|\mathbf{K}_n+\mathbf{k}|s) +\lambda[j_0(\kappa_n(\mathbf{k})s)]^{-1}\sum_{n'\neq n}[|\mathbf{K}_{n'}+\mathbf{k}|^2-|\mathbf{K}_n+\mathbf{k}|^2-\lambda\varepsilon_n(\mathbf{k})]^{-1}j_0(|\mathbf{K}_{n'}+\mathbf{k}|s) . \quad (29)$$

The lowest-order terms in (29) are independent of λ and sufficient to determine $\varepsilon_n(\mathbf{k})$. For nondegenerate eigenvalues with $|\mathbf{K}_{n'}+\mathbf{k}| \neq |\mathbf{K}_n+\mathbf{k}|$ follows

$$0=1-[\varepsilon_n(\mathbf{k})j_0(\kappa_n(\mathbf{k})s)^{-1}j_0(|\mathbf{K}_n+\mathbf{k}|s)$$
$$=1-[\varepsilon_n(\mathbf{k})]^{-1}, \tag{30}$$

where the equivalence of $\kappa_n(\mathbf{k})$ and $|\mathbf{K}_n+\mathbf{k}|$ to lowest order in λ has been used. This leads to $\varepsilon_n(\mathbf{k})=1$ and the ansatz (28) reproduces the exact result (1). Degenerate eigenvalues arising from the symmetry of the underlying lattice do not pose a problem because the constant potential does not change the symmetry and does not lift the degeneracies. The above derivation can be repeated for each irreducible representation of the symmetry group, leading always to the result (1).

It should be emphasized that the derivation given in this section is only valid if both conditions $r<|\mathbf{r}-\mathbf{R}_m|$ and $r<R_m$ are satisfied. This puts certain restrictions on the construction of the unit cells around the cell centers R_m. The first condition means that the cells must be separated by planes bisecting perpendicularly the straight-line connections between cell centers, i.e., by using the Wigner-Seitz construction. The second condition does not allow too small distances between lattice points in one direction together with too large distances in other directions.

IV. STUDY OF THE l CONVERGENCE

For applications of multiple-scattering theory to electronic-structure calculations, it is very important that the results rapidly converge with $l_{\max}$, the maximum number of angular momenta used. For simplicity the present consideration is restricted to the first-order term (20), which is justified for two reasons. First, in the Appendix it is shown that second-, third-, and presumably all higher-order terms vanish and, secondly, the residual error in Faulkner's numerical investigation[24] is rather obviously proportional to λ. By using (A2.5) of Ref. 2 and by noting that $A_{lm;l'm'}$ of Ref. 2 is equivalent to $g_{LL'}(\mathbf{k},E)-i\kappa\delta_{LL'}$, the following result is easily obtained,

$$\lambda g_{LL'}(\mathbf{k},E)=\lambda\kappa\delta_{LL'}[i-n_l(\kappa s')/j_l(\kappa s)]-\lambda(4\pi)^2 i^{l-l'}[\tau j_l(\kappa s)j_{l'}(\kappa s')]^{-1}$$
$$\times\sum_{n'}(|\mathbf{K}_{n'}+\mathbf{k}|^2-E)^{-1}j_l(|\mathbf{K}_{n'}+\mathbf{k}|s)j_{l'}(|\mathbf{K}_{n'}+\mathbf{k}|s')Y_L(\mathbf{k}_{n'})Y_{L'}(\mathbf{k}_{n'}), \tag{31}$$

where $\mathbf{k}_{n'}$ is abbreviated as $(\mathbf{K}_{n'}+\mathbf{k})/|\mathbf{K}_{n'}+\mathbf{k}|$ and where s and s' are arbitrary provided that $s<s'$ and provided that s' is smaller than the muffin-tin radius. By use of the ansatz (28) and by the arguments which led to (30) follows

$$\lambda g_{LL'}(\mathbf{k},E_n(\mathbf{k}))\simeq(4\pi)^2 i^{l-l'}[\tau\varepsilon_n(\mathbf{k})]^{-1}Y_L(\mathbf{k}_n)Y_{L'}(\mathbf{k}_n), \tag{32}$$

where only terms of zeroth order in λ are retained on the right-hand side. Implementing this result in the condition (20) and using (19) leads to

$$\varepsilon_n(\mathbf{k})=\tau^{-1}\int_\tau d\mathbf{r}\left|4\pi\sum_L i^l Y_L(\mathbf{k}_n)J_L(\mathbf{r},|\mathbf{K}_n+\mathbf{k}|)\right|^2, \tag{33}$$

which, upon summation over L, leads to

$$\varepsilon_n(\mathbf{k})=\tau^{-1}\int_\tau d\mathbf{r}\,|\exp[i(\mathbf{K}_n+\mathbf{k})\cdot\mathbf{r}]|^2=1. \tag{34}$$

This result is very similar to the usual first-order perturbation result for the bound states of the empty lattice with constant potential, except that the integration is over the unit cell instead of over the entire crystal and that the plane waves are accordingly normalized. Expression (33) contains the usual angular-momentum expansion[27] for the plane wave $\exp[i(\mathbf{K}_n+\mathbf{k})\cdot\mathbf{r}]$ and converges with $l_{\max}$ as the Taylor expansion for the exponential function e^x, i.e., rapidly if the argument $x=|\mathbf{K}_n+\mathbf{k}|r$ is not too large. The actual convergence is now studied for a particular example of a two-dimensional lattice. This example is chosen because the integral in (33) with a truncated sum is more easily performed in two dimensions and because Faulkner[24] investigated the same case. The main differences from the three-dimensional case are that spherical Bessel and Hankel functions j_l and $h_l^{(1)}$ are replaced by Bessel and Hankel functions J_l and $H_l^{(1)}$ of integer order and that the spherical harmonics are replaced by "circular" harmonics which are simple exponentials. For a two-dimensional square lattice with lattice constant $a=2\pi$, i.e., the example considered by Faulkner,[24] the first-order result for the t matrix can be written as

$$t_{ll'}^{(1)}(E)=\int_{-\pi}^{\pi}dx\int_{-\pi}^{\pi}dy\,\exp[i(l+l')\phi]J_l(\kappa r)J_{l'}(\kappa r)$$
$$=\int_0^{\pi}dr\,r\,J_l(\kappa r)J_{l'}(\kappa r)\int_0^{2\pi}d\phi\exp[i(l+l')\phi]+\int_{\pi}^{\pi\sqrt{2}}dr\,r\,J_l(\kappa r)J_{l'}(\kappa r)\int d\phi\exp[i(l+l')\phi], \tag{35}$$

where the polar coordinates $x=r\cos\phi$ and $y=r\sin\phi$ have been used and where the last $d\phi$ integral is over the four intervals

$$\arccos(\pi/r)+\nu\pi/2\leq\phi\leq(\nu+1)\pi/2-\arccos(\pi/r)\quad\text{with }\nu=0,1,2,3. \tag{36}$$

By the fourfold symmetry, $t_{ll'}(E)$ vanishes, except for $l+l'=4\mu$ with arbitrary integer μ, and the last $d\phi$ integral in (35) can be replaced by 4 times the integral over the interval with $v=0$. By trivial integration over $d\phi$ follows

$$t_{ll'}^{(1)}(E)=2\pi\int_0^{\pi\sqrt{2}}dr\,r\,J_l(\kappa r)J_{l'}(\kappa r)-8\int_{\pi}^{\pi\sqrt{2}}dr\,r\,J_l(\kappa r)J_{l'}(\kappa r)\arccos(\pi/r)\quad\text{for } l+l'=0 \tag{37}$$

and

$$t_{ll'}^{(1)}(E)=-8/(l+l')\int_{\pi}^{\pi\sqrt{2}}dr\,r\,J_l(\kappa r)J_{l'}(\kappa r)\sin[(l+l')\arccos(\pi/r)]\quad\text{for } l+l'=4\mu\neq 0\ . \tag{38}$$

Because of $J_l(\kappa r)=(-1)^l J_{-l}(\kappa r)$, it is possible to choose the order of the Bessel functions always positive and to apply a convenient expression[27] for their products,

$$J_l(\kappa r)J_{l'}(\kappa r)=(\kappa r/2)^{l+l'}\sum_{p\geq 0}(-1)^p(\kappa r/2)^{2p}(l+l'+2p)!/[p!(l+l'+p)!(l+p)!(l'+p)!]\ , \tag{39}$$

which is valid if $l\geq 0$ and $l'\geq 0$. The remaining integrals in (37) and (38) are easily performed numerically, e.g., by Simpson integration to any desired accuracy.

It is interesting to compare the results obtained by (33) with ones presented by Faulkner,[24] who had to use much more involved computations. The eigenvalues studied by him were for the case $\mathbf{k}=\mathbf{0}$ and for $|\mathbf{K}_n|=1.0$. The p- and d-like eigenstates had rapidly converging eigenvalues (agreement of six figures with the exact results were obtained with $l_{\max}=34$), whereas the s-like eigenstate had a slowly converging eigenvalue. Even with $l_{\max}=56$ Faulkner could not decide whether near-field corrections were necessary or not. From symmetry arguments the eigenvalue for the s-like eigenstate can be obtained by using 4 times the right-hand side of (33) and by restricting the sum over l to multiples of 4. In Fig. 1 the results obtained for different values of $l_{\max}$ are shown together with the results of Ref. 24. The present results (stars) clearly converge much better than those of Ref. 24 (circles). Deviations from the exact result ($1-\varepsilon=0$) can only be seen for $l_{\max}=0$ and 4. At first sight, the discrepancy between Ref. 24 and the present paper is rather puzzling but it has a simple reason. It arises from the particular form of the secular matrix used in the calculations. Here $1-gt$ is chosen and t is truncated, whereas Faulkner[23] chose $CS^{-1}+B$ and truncated CS^{-1}. Without the truncation the two forms are completely equivalent because CS^{-1} is the negative of the real part of t^{-1} and B is the real part of g, but with the truncation they lead to quite different results. Also, with the present expansion in λ it is possible to proceed as Faulkner and to obtain less rapidly convergent results. The first-order t matrix (35) must be calculated with a rather large cutoff ($l=124$ is chosen here and by Faulkner) such that its inverse becomes a good approximation for t^{-1}. The matrix t^{-1} can be truncated equivalently to Faulkner with different values of $l_{\max}$ and the inverse of the truncated t^{-1} can be used as an approximation for t in condition (20). The results are shown in Table I. The first two columns are directly obtained from (33) and represent an average over the symmetrized eigenvalues that would be obtained as actual output from a band-structure calculation. Obviously, the values obtained by truncating t (present work) converge much more rapidly than those obtained by truncating t^{-1} (proceeding similarly to Faulkner). The last two columns in Table I contain the symmetrized results for the s-like eigenstate for which only $l=0,4,8,12,\ldots$ contribute. These results are shown in Fig. 1 by stars (if truncating t) and by crosses (if truncating t^{-1}). The values obtained by truncating t^{-1} compare very favorably with Faulkner's values,[24] particularly if one considers that he used $\lambda=-0.2$ and -0.4, whereas the present calculations are for the limit $\lambda\to 0$. For $l_{\max}<20$ the present results can be directly estimated from extrapolating Faulkner's values for $\lambda=-0.4$ and -0.2 to $\lambda=0.0$. For $l_{\max}>20$ Faulkner had considerable numerical difficulties obtaining S^{-1} because det$S$ becomes very small. It should be noted that the truncation problem mentioned

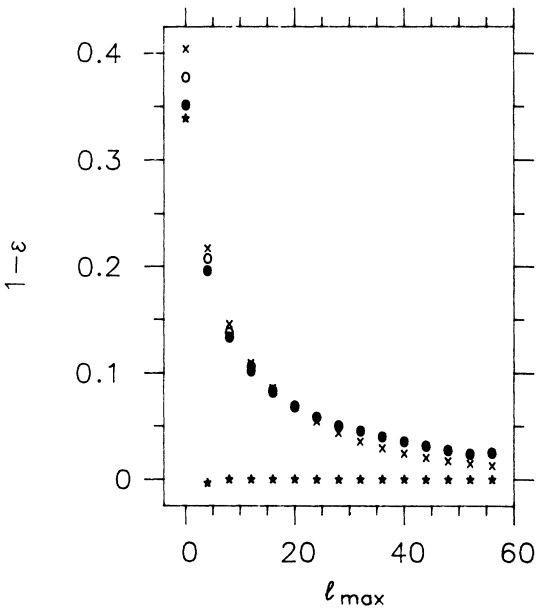

FIG. 1. Relative error for the eigenvalue of the s-like eigenstate at $|\mathbf{K}_n+\mathbf{k}|=1.0$ in the two-dimensional square lattice with lattice constant 2π. The results obtained by truncating (33) are shown by stars and the results obtained by truncating t^{-1} are shown by crosses. These results (valid in the limit $\lambda\to 0$) are compared with Faulkner's results (Ref. 24) for $\lambda=-0.20$ (open circles) and for $\lambda=-0.4$ (solid circles).

TABLE I. Averaged relative error for the eigenvalues and relative error for the s-like eigenstate at $|\mathbf{K}_n+\mathbf{k}|=1.0$ in the two-dimensional square lattice with lattice constant 2π. The results obtained by truncating (33) are shown together with those obtained as described in the text by a procedure similar to Ref. 24. Note the rapid convergence of the present results.

	Averaged error		Error for s-like state	
$l_{\max}$	Present	Ref. 24	Present	Ref. 24
0	0.835	0.851	0.339	0.404
1	0.423	0.482		
2	0.209	0.244		
3	0.0699	0.138		
4	−0.0157	0.0915	−0.003 29	0.217
5	−0.006 09	0.0907		
6	−0.002 49	0.0818		
7	−0.000 810	0.0667		
8	−0.000 012 2	0.0489	0.000 003 79	0.146
9	0.000 006 63	0.0489		
10	0.000 002 84	0.0474		
11	0.000 000 94	0.0427		
12	0.000 000 00	0.0335	0.000 000 00	0.109
20		0.0193		0.068
40		0.00633		0.024
60		0.00285		0.011

here does not occur for muffin-tin potentials for which the matrices t and t^{-1} are diagonal. It is therefore a problem only appearing in non-muffin-tin multiple-scattering equations.

V. DISCUSSION AND CONCLUSION

It is easy to establish the connection between the single-site wave function $R_L(\mathbf{r},E)$ used here and in Ref. 17 and the single-site wave function $\Phi_L(\mathbf{r},E)$ used by other authors.[13,14,20] Equation (2.5) in Ref. 13 reads

$$\Phi_{L'}(\mathbf{r},E)=\sum_L J_L(\mathbf{r},E)C_{LL'} + \int_\tau d\mathbf{r}'\mathrm{Re}[g(\mathbf{r}-\mathbf{r}',E)]v(\mathbf{r}')\Phi_{L'}(\mathbf{r}',E)\ . \tag{40}$$

Contrary to (2), the last equation contains only the real part of the free-space Green's function. The imaginary part can be obtained from (24) as

$$\mathrm{Im}[g(\mathbf{r}-\mathbf{r}',E)]=-\kappa\sum_L J_L(\mathbf{r},E)J_L(\mathbf{r}',E)\ , \tag{41}$$

which leads to

$$\begin{aligned}\int_\tau d\mathbf{r}'\mathrm{Im}[g(\mathbf{r}-\mathbf{r}',E)]v(\mathbf{r}')\Phi_{L'}(\mathbf{r}',E) &= -\kappa\sum_L J_L(\mathbf{r},E)\int_\tau d\mathbf{r}'J_L(\mathbf{r}',E)v(\mathbf{r}')\Phi_{L'}(\mathbf{r}',E)\\ &=\kappa\sum_L J_L(\mathbf{r},E)S_{LL'}\ ,\end{aligned} \tag{42}$$

with the notation $-S_{LL'}$ for the last integral as introduced in (3.4) of Ref. 13. By use of (42), one can rewrite (40) for the special case of a constant potential $v(\mathbf{r}')=\lambda$ as

$$\Phi_{L'}(\mathbf{r},E)=\sum_L J_L(\mathbf{r},E)(C_{LL'}-i\kappa S_{LL'}) +\lambda\int_\tau d\mathbf{r}'g(\mathbf{r}-\mathbf{r}',E)\Phi_{L'}(\mathbf{r}',E)\ . \tag{43}$$

Comparison with (2) shows that $\Phi_{L'}$ can be identified as $\sum_L R_L(C_{LL'}-i\kappa S_{LL'})$. Inserting this into the definition of $S_{LL'}$ leads to

$$\begin{aligned}S_{LL'}&=-\lambda\int_\tau d\mathbf{r}\,J_L(\mathbf{r},E)\Phi_{L'}(\mathbf{r},E)\\ &=-\lambda\sum_{L''}\int_\tau d\mathbf{r}\,J_L(\mathbf{r},E)R_{L''}(\mathbf{r},E)(C_{L''L'}-i\kappa S_{L''L'})\ ,\end{aligned} \tag{44}$$

and using (4) leads to

$$S_{LL'}=-\sum_{L''}t_{LL''}(C_{L''L'}-i\kappa S_{L''L'})\ , \tag{45}$$

from which $t^{-1}=-CS^{-1}+i\kappa$ follows. Faulkner[20,23,24] denotes the matrix CS^{-1} by X and Williams and van Morgan[13] by η, whereas Gonis[15] uses the notation m for t^{-1}. This consideration shows that the multiple-scattering equations used here and in Refs. 12, 13, 15, 17, and 24 are equivalent provided that the angular-momentum expansion is not truncated. On the other hand, Brown and Ciftan[14,21,22] define a wave function $\Phi^S_{L'}(\mathbf{r},E)$ by using (40) with the integral extended to a sphere which bounds the unit cell. They then use this wave function to calculate C^Ω and S^Ω, which differ from C and S defined by Williams and van Morgan.[12,13] In the present notation the procedure of Brown and Ciftan is equivalent to calculating $R^S_L(\mathbf{r},E)$ from (2) with the integral extended to the bounding sphere and using

$$R^\Omega_L(\mathbf{r},E)=J_L(\mathbf{r},E)+\lambda\int_\tau d\mathbf{r}'g(\mathbf{r}-\mathbf{r}',E)R^S_L(\mathbf{r}',E) \tag{46}$$

as an approximation for $R_L(\mathbf{r},E)$. An expansion of R_L^{Ω} agrees with that for R_L to zeroth and first order in λ. The second order differs and leads to a difference in third order for the t matrix,

$$t_{LL'}^{\Omega(3)}(E)=\int_\tau d\mathbf{r}\int_\tau d\mathbf{r}'\int_S d\mathbf{r}''J_L(\mathbf{r},E)g(\mathbf{r}-\mathbf{r}'',E)\times g(\mathbf{r}''-\mathbf{r}',E)J_{L'}(\mathbf{r}',E)\ , \quad (47)$$

which is equal to (A4), except that the $d\mathbf{r}''$ integration is over the bounding sphere instead of the unit cell. With (47) the result (A16) cannot be obtained because the sum of integrals over bounding spheres is not equal to the integral over all space. This prevents application of (A14) and the derivation of the Appendix breaks down. As a result the eigenvalues obtained by the multiple-scattering equations of Brown and Ciftan are likely to show deviations from the exact values (1) in the third order of λ. Because the third-order terms are very small for the test cases studied in the literature,[21–24] it is clear that no discrimination between the different formulations could be made on a numerical basis. A final remark can be added concerning the atomic-sphere approximation, where the integrals over unit cells are approximated by integrals over spheres of equal volume. To first order in λ the exact results is obtained, as (34) easily reveals. Second and higher orders deviate because the integral over all spheres is not equal to the integral over all space and (A15) cannot be obtained.

In conclusion, it is worth summarizing with the following points.

(1) An expansion with the magnitude of the constant potential as an expansion parameter has been made for the empty-lattice model and it has been shown that the multiple-scattering equations given in Ref. 17 lead to a first-order term which is the exact result, and that second- and third-order terms vanish identically. It is very likely that this is also true for higher-order terms.

(2) It has been shown that the eigenvalues converge exponentially with the number of angular-momentum components taken into account. $l=4$ or 6 appears to be sufficient for practical purposes. This is in contrast to the common belief that the convergence is very slow.

(3) The multiple-scattering equations given by Williams and van Morgan[12,13] and similarly by Faulkner[20] and Gonis[15] are equivalent, but suffer from the form of the secular matrix if the angular-momentum expansion is truncated. The results are much less rapidly converging. The equations given by Brown and Ciftan[14] are not exact, but represent a good approximation.

(4) For the derivations in the present paper as well as for those in Ref. 17, certain conditions for dividing space into cells must be satisfied. They are stated at the end of Sec. III as the Wigner-Seitz construction together with $r<R_m$. It seems likely that the cells around the atomic positions cannot be constructed otherwise without introducing divergencies for $l_{\max}\to\infty$. For practical applications this is not problematic because the conditions can always be satisfied by introducing additional empty cells.

(5) It is an important question as to whether or not the results found here for the special case of the empty lattice, i.e., rapid l convergence and negligible near-field effects, are generally valid also for arbitrary smooth potentials. The present work supports this view because a nonconstant potential represents a minor difficulty compared to the complicated nonspherical geometry for the single-scattering event which already occurs in the empty-lattice case. Nevertheless, further work is really desirable to investigate this point because rapid convergence and insignificant near-field effects would allow one to use multiple-scattering theory in electronic-structure calculations not limited by the muffin-tin approximation, e.g., for not closely packed materials, surfaces, and interfaces.

APPENDIX: SECOND- AND THIRD-ORDER EXPANSION

The result for the single-site t matrix (4) to third order in λ is obtained from (11)–(13) as

$$t_{LL'}(E)=\lambda t_{LL'}^{(1)}(E)+\lambda^2 t_{LL'}^{(2)}(E)+\lambda^3 t_{LL'}^{(3)}(E)\ , \quad (A1)$$

with

$$t_{LL'}^{(1)}(E)=\int_\tau d\mathbf{r}\,J_L(\mathbf{r},E)J_{L'}(\mathbf{r},E)\ , \quad (A2)$$

$$t_{LL'}^{(2)}(E)=\int_\tau d\mathbf{r}\int_\tau d\mathbf{r}'J_L(\mathbf{r},E)g(\mathbf{r}-\mathbf{r}',E)J_{L'}(\mathbf{r}',E)\ , \quad (A3)$$

$$t_{LL'}^{(3)}(E)=\int_\tau d\mathbf{r}\int_\tau d\mathbf{r}'\int_\tau d\mathbf{r}''J_L(\mathbf{r},E)g(\mathbf{r}-\mathbf{r}'',E)\times g(\mathbf{r}''-\mathbf{r}',E)J_{L'}(\mathbf{r}',E)\ . \quad (A4)$$

The KKR determinant follows from (14)–(17) as

$$\begin{aligned}\det|1-gt| =& 1-\lambda\,\mathrm{Tr}(gt^{(1)})+(\lambda^2/2)\{-2\,\mathrm{Tr}(gt^{(2)})+[\mathrm{Tr}(gt^{(1)})]^2-\mathrm{Tr}(gt^{(1)}gt^{(1)})\}\\ &-(\lambda^3/6)[6\,\mathrm{Tr}(gt^{(3)})+6\,\mathrm{Tr}(gt^{(2)}gt^{(1)})+2\,\mathrm{Tr}(gt^{(1)}gt^{(1)}gt^{(1)})]\\ &-(\lambda^3/6)\mathrm{Tr}(gt^{(1)})\{[\mathrm{Tr}(gt^{(1)})]^2-6\,\mathrm{Tr}(gt^{(2)})-3\,\mathrm{Tr}(gt^{(1)}gt^{(1)})\}\end{aligned} \quad (A5)$$

in matrix notation with $g=g_{LL'}(\mathbf{k},E)$ and $t^{(i)}=t_{LL'}^{(i)}(E)$. The sums over the angular-momentum indices in (A5) can be performed by using (6) and the addition theorems (22)–(24). The term proportional to λ has already been derived in (25) as

$$\mathrm{Tr}(gt^{(1)})=\tau\sum_{m\neq 0}\exp(i\mathbf{k}\cdot\mathbf{R}_m)g(R_m,E)\ . \quad (A6)$$

The other traces in (A5) are obtained by repeatedly using the result

$$\sum_{L,L'} g_{LL'}^{(m)}(E)\int_\tau d\mathbf{r}\int_\tau d\mathbf{r}' f(\mathbf{r},\mathbf{r}')J_L(\mathbf{r},E)J_{L'}(\mathbf{r}',E)=\int_\tau d\mathbf{r}\int_\tau d\mathbf{r}' f(\mathbf{r},\mathbf{r}')g(\mathbf{r}'-\mathbf{r}+\mathbf{R}_m,E)\ , \tag{A7}$$

which can be established for arbitrary functions $f(\mathbf{r},\mathbf{r}')$ by splitting the double integral $\int d\mathbf{r}\int d\mathbf{r}'$ into two integrals, one over $r'\le r$ and the other over $r'\ge r$, and by interchanging $\mathbf{r}$ and $\mathbf{r}'$ in the second integral. This leads, for the left-hand side of (A7), to

$$\sum_{L,L'} g_{LL'}^{(m)}(E)\int_\tau d\mathbf{r}\int_{r'\le r} d\mathbf{r}'[f(\mathbf{r},\mathbf{r}')J_L(\mathbf{r},E)J_{L'}(\mathbf{r}',E)+f(\mathbf{r}',\mathbf{r})J_{L'}(\mathbf{r},E)J_L(\mathbf{r}',E)]$$

by using (22) and (23) to

$$-i\kappa\int_\tau d\mathbf{r}\int_{r'\le r} d\mathbf{r}'\left[f(\mathbf{r},\mathbf{r}')\sum_{L'} H_{L'}(\mathbf{r}-\mathbf{R}_m,E)J_{L'}(\mathbf{r}',E)+f(\mathbf{r}',\mathbf{r})\sum_L H_L(\mathbf{r}+\mathbf{R}_m,E)J_L(\mathbf{r}',E)\right]\ ,$$

and by using (24) with $\mathbf{r}$ replaced by $\mathbf{r}'$ and $\mathbf{R}_m$ replaced by $\mathbf{r}-\mathbf{R}_m$ or $\mathbf{r}+\mathbf{R}_m$ to

$$\int_\tau d\mathbf{r}\int_{r'\le r} d\mathbf{r}'[f(\mathbf{r},\mathbf{r}')g(\mathbf{r}'-\mathbf{r}+R_m,E)+f(\mathbf{r}',\mathbf{r})g(\mathbf{r}'-\mathbf{r}-\mathbf{R}_m,E)]\ ,$$

which is equal to the right-hand side of (A7) because of $g(\mathbf{r},E)=g(r,E)$. The necessary conditions $r'<|\mathbf{r}-\mathbf{R}_m|$ and $r'<|\mathbf{r}+\mathbf{R}_m|$ are satisfied because of $r'\le r$ and because the conditions $r<|\mathbf{r}-\mathbf{R}_m|$ and $r<|\mathbf{r}+\mathbf{R}_m|$ are satisfied provided Wigner-Seitz cells are used. By using (A7) the following results are obtained:

$$\mathrm{Tr}(gt^{(2)})=\sum_{m\neq 0}\exp(i\mathbf{k}\cdot\mathbf{R}_m)\int_\tau d\mathbf{r}\int_\tau d\mathbf{r}' g(\mathbf{r}-\mathbf{r}',E)g(\mathbf{r}'-\mathbf{r}+\mathbf{R}_m,E)\ , \tag{A8}$$

$$\mathrm{Tr}(gt^{(3)})=\sum_{m\neq 0}\exp(i\mathbf{k}\cdot\mathbf{R}_m)\int_\tau d\mathbf{r}\int_\tau d\mathbf{r}'\int_\tau d\mathbf{r}'' g(\mathbf{r}-\mathbf{r}'',E)g(\mathbf{r}''-\mathbf{r}',E)g(\mathbf{r}'-\mathbf{r}+\mathbf{R}_m,E)\ , \tag{A9}$$

$$\mathrm{Tr}(gt^{(1)}gt^{(1)})=\sum_{m\neq 0,\,m'\neq 0}\exp[i\mathbf{k}\cdot(\mathbf{R}_m+\mathbf{R}_{m'})]\int_\tau d\mathbf{r}\int_\tau d\mathbf{r}' g(\mathbf{r}'-\mathbf{r}-\mathbf{R}_m,E)g(\mathbf{r}'-\mathbf{r}+\mathbf{R}_m,E)\ , \tag{A10}$$

$$\mathrm{Tr}(gt^{(2)}gt^{(1)})=\sum_{m\neq 0,\,m'\neq 0}\exp[i\mathbf{k}\cdot(\mathbf{R}_m+\mathbf{R}_{m'})]\int_\tau d\mathbf{r}\int_\tau d\mathbf{r}'\int_\tau d\mathbf{r}'' g(\mathbf{r}-\mathbf{r}'',E)g(\mathbf{r}-\mathbf{r}'-\mathbf{R}_m,E)g(\mathbf{r}'-\mathbf{r}''-\mathbf{R}_{m'},E)\ , \tag{A11}$$

$$\mathrm{Tr}(gt^{(1)}gt^{(1)}gt^{(1)})=\sum_{m\neq 0,\,m'\neq 0,\,m''\neq 0}\exp[i\mathbf{k}\cdot(\mathbf{R}_m+\mathbf{R}_{m'}+\mathbf{R}_{m''})]\times\int_\tau d\mathbf{r}\int_\tau d\mathbf{r}'\int_\tau d\mathbf{r}'' g(\mathbf{r}-\mathbf{r}'-\mathbf{R}_{m'},E)g(\mathbf{r}'-\mathbf{r}''-\mathbf{R}_{m''},E)g(\mathbf{r}''-\mathbf{r}-\mathbf{R}_m,E)\ . \tag{A12}$$

The terms (A8) and (A10) can be combined to yield

$$\begin{aligned}2\,\mathrm{Tr}(gt^{(2)})+\mathrm{Tr}(gt^{(1)}gt^{(1)})&=\sum_{m,m'}\exp[i\mathbf{k}\cdot(\mathbf{R}_m+\mathbf{R}_{m'})]\int_\tau d\mathbf{r}\int_\tau d\mathbf{r}' g(\mathbf{r}'-\mathbf{r}-\mathbf{R}_m,E)g(\mathbf{r}'-\mathbf{r}+\mathbf{R}_{m'},E)\\&\quad-\int_\tau d\mathbf{r}\int_\tau d\mathbf{r}' g(\mathbf{r}'-\mathbf{r},E)g(\mathbf{r}'-\mathbf{r},E)\\&=\sum_{m''}\exp(i\mathbf{k}\cdot\mathbf{R}_{m''})\int_\tau d\mathbf{r}\sum_m\int_\tau d\mathbf{r}' g(\mathbf{r}'-\mathbf{r}-\mathbf{R}_m,E)g(\mathbf{r}'-\mathbf{r}+\mathbf{R}_{m''}-\mathbf{R}_m,E)\\&\quad-\int_\tau d\mathbf{r}\int_\tau d\mathbf{r}' g(\mathbf{r}'-\mathbf{r},E)g(\mathbf{r}'-\mathbf{r},E)\ ,\end{aligned} \tag{A13}$$

which is obtained by renaming $\mathbf{R}_m+\mathbf{R}_{m'}$ as $\mathbf{R}_{m''}$. The sum over m and the integration $d\mathbf{r}'$ over the unit cell can be combined into an integration over all space, and the general Green's-function identity

$$\partial_E g(\mathbf{r}-\mathbf{r}',E)=-\int_\infty d\mathbf{r}'' g(\mathbf{r}''-\mathbf{r},E)g(\mathbf{r}''-\mathbf{r}',E) \tag{A14}$$

can be used to rewrite (A13) as

$$2\,\mathrm{Tr}(gt^{(2)})+\mathrm{Tr}(gt^{(1)}gt^{(1)})=-\tau\sum_{m''}\exp(i\mathbf{k}\cdot\mathbf{R}_{m''})\partial_E g(R_{m''},E)-\int_\tau d\mathbf{r}'\int_\tau d\mathbf{r}\, g(\mathbf{r}-\mathbf{r}',E)g(\mathbf{r}-\mathbf{r}',E)\ . \tag{A15}$$

Similarly, the terms (A9), (A11), and (A12) can be combined to yield

$$
\begin{aligned}
&6\,\mathrm{Tr}(gt^{(3)})+6\,\mathrm{Tr}(gt^{(2)}gt^{(1)})+2\,\mathrm{Tr}(gt^{(1)}gt^{(1)}gt^{(1)}) \\
&\quad=2\sum_{m,m',m''}\exp[i\mathbf{k}\cdot(\mathbf{R}_m+\mathbf{R}_{m'}+\mathbf{R}_{m''})] \\
&\qquad\qquad\times\int_\tau d\mathbf{r}\int_\tau d\mathbf{r}'\int_\tau d\mathbf{r}''g(\mathbf{r}-\mathbf{r}'-\mathbf{R}_{m'},E)g(\mathbf{r}'-\mathbf{r}''-\mathbf{R}_{m''},E)g(\mathbf{r}''-\mathbf{r}-\mathbf{R}_m,E) \\
&\quad-2\int_\tau d\mathbf{r}\int_\tau d\mathbf{r}'\int_\tau d\mathbf{r}''g(\mathbf{r}-\mathbf{r}'',E)g(\mathbf{r}'-\mathbf{r}'',E)g(\mathbf{r}''-\mathbf{r},E) \\
&\quad=\tau\sum_{m'''}\exp(i\mathbf{k}\cdot\mathbf{R}_{m'''})\partial_E^2 g(R_{m'''},E)-2\int_\tau d\mathbf{r}\int_\tau d\mathbf{r}'\int_\tau d\mathbf{r}''g(\mathbf{r}-\mathbf{r}'',E)g(\mathbf{r}'-\mathbf{r}'',E)g(\mathbf{r}''-\mathbf{r},E)\ , \qquad \text{(A16)}
\end{aligned}
$$

where the last result is obtained by renaming $\mathbf{R}_m+\mathbf{R}_{m'}+\mathbf{R}_{m''}$ as $\mathbf{R}_{m'''}$ and by using (A14) twice. With the abbreviations

$$
\begin{aligned}
G_1(E)&=\tau\sum_{m\neq 0}\exp(i\mathbf{k}\cdot\mathbf{R}_m)g(R_m,E) \\
&=(\tau\kappa/4\pi)[i+\cot(\kappa s)/\sqrt{4\pi}]-[j_0(\kappa s)]^{-1}\sum_{n'}(\,|\,\mathbf{K}_{n'}+\mathbf{k}\,|^2-E)^{-1}j_0(\,|\,\mathbf{K}_{n'}+\mathbf{k}\,|\,s)\ , \qquad \text{(A17)}
\end{aligned}
$$

$$
G_2(E)=\tau\sum_m\exp(i\mathbf{k}\cdot\mathbf{R}_m)\partial_E g(R_m,E)=-\sum_{n'}(\,|\,\mathbf{K}_{n'}+\mathbf{k}\,|^2-E)^{-2}\ , \qquad \text{(A18)}
$$

$$
G_3(E)=\tau\sum_m\exp(i\mathbf{k}\cdot\mathbf{R}_m)\partial_E^2 g(R_m,E)=2\sum_{n'}(\,|\,\mathbf{K}_{n'}+\mathbf{k}\,|^2-E)^{-3} \qquad \text{(A19)}
$$

finally follows, up to second order in λ,

$$
\det|\,1-gt\,|=1-\lambda G_1(E)+(\lambda^2/2)[G_1^2(E)+G_2(E)]+(\lambda^2/2)\int_\tau d\mathbf{r}'\int_\tau d\mathbf{r}\,g(\mathbf{r}-\mathbf{r}',E)g(\mathbf{r}-\mathbf{r}',E)\ , \qquad \text{(A20)}
$$

and, up to third order in λ,

$$
\begin{aligned}
\det|\,1-gt\,|&=1-\lambda G_1(E)+(\lambda^2/2)[G_1^2(E)+G_2(E)]-(\lambda^3/6)[G_1^3(E)+3G_1(E)G_2(E)+G_3(E)] \\
&\quad+[\lambda^2/2-(\lambda^3/2)G_1(E)]\int_\tau d\mathbf{r}'\int_\tau d\mathbf{r}\,g(\mathbf{r}-\mathbf{r}',E)g(\mathbf{r}-\mathbf{r}',E) \\
&\quad+(\lambda^3/3)\int_\tau d\mathbf{r}\int_\tau d\mathbf{r}'\int_\tau d\mathbf{r}''g(\mathbf{r}-\mathbf{r}'',E)g(\mathbf{r}'-\mathbf{r}'',E)g(\mathbf{r}''-\mathbf{r},E)\ . \qquad \text{(A21)}
\end{aligned}
$$

To establish the result (1) up to third order in λ, it must be shown that the ansatz $E_n(\mathbf{k})=|\,\mathbf{K}_n+\mathbf{k}\,|^2+\lambda+\lambda^2\zeta+\lambda^3\zeta'$ for the eigenvalues—if inserted into $\det|\,1-gt\,|=0$—leads to $\zeta=0$ and $\zeta'=0$. Instead of using (A21) to determine both ζ and ζ' it is easier to use first (A20) to determine ζ and then (A21) to determine ζ'. Equation (A20) leads to

$$
0=\tfrac{1}{2}+(\lambda^2/2)G_2(E_n(\mathbf{k}))+\tfrac{1}{2}[1-\lambda G_1(E_n(\mathbf{k}))]^2+(\lambda^2/2)\int_\tau d\mathbf{r}'\int_\tau d\mathbf{r}\,g(\mathbf{r}-\mathbf{r}',E_n(\mathbf{k}))g(\mathbf{r}-\mathbf{r}',E_n(\mathbf{k}))\ . \qquad \text{(A22)}
$$

To obtain ζ it is sufficient to retain terms independent of λ and proportional to λ in (A22). By the first-order result, the expression $1-\lambda G_1(E_n(\mathbf{k}))$ is at least proportional to λ and the last two terms in (A22) can be neglected. Expanding (A18) leads to

$$
\begin{aligned}
0&=\tfrac{1}{2}+(\lambda^2/2)\left[(\lambda+\lambda^2\zeta)^{-2}-\sum_{n'\neq n}(\,|\,\mathbf{K}_{n'}+\mathbf{k}\,|^2-|\,\mathbf{K}_n+\mathbf{k}\,|^2-\lambda-\lambda^2\zeta)^{-2}\right] \\
&=-\lambda\zeta+\text{terms of higher order than first in }\lambda\ . \qquad \text{(A23)}
\end{aligned}
$$

This implies $\zeta=0$. Similarly, (A21) leads to

$$
\begin{aligned}
0&=\tfrac{1}{3}-(\lambda^3/6)G_3(E_n(\mathbf{k}))-\tfrac{1}{3}[1-\lambda G_1(E_n(\mathbf{k}))]^3 \\
&\quad+[1-\lambda G_1(E_n(\mathbf{k}))][1-\lambda G_1(E_n(\mathbf{k}))]+(\lambda^2/2)[G_1^2(E_n(\mathbf{k}))+G_2(E_n(\mathbf{k}))] \\
&\quad+(\lambda^2/2)[1-\lambda G_1(E_n(\mathbf{k}))\int_\tau d\mathbf{r}'\int_\tau d\mathbf{r}\,g(\mathbf{r}-\mathbf{r}',E_n(\mathbf{k}))g(\mathbf{r}-\mathbf{r}',E_n(\mathbf{k})) \\
&\quad+(\lambda^3/3)\int_\tau d\mathbf{r}\int_\tau d\mathbf{r}'\int_\tau d\mathbf{r}''g(\mathbf{r}-\mathbf{r}'',E_n(\mathbf{k}))g(\mathbf{r}'-\mathbf{r}'',E_n(\mathbf{k}))g(\mathbf{r}''-\mathbf{r},E_n(\mathbf{k}))\ . \qquad \text{(A24)}
\end{aligned}
$$

Here all terms but the first two can be neglected because they are at least proportional to λ^3. Expanding (A19) leads to

$$
\begin{aligned}
0&=\tfrac{1}{3}-(\lambda^3/3)\left[(\lambda+\lambda^3\zeta')^{-3}+\sum_{n'\neq n}(\,|\,\mathbf{K}_{n'}+\mathbf{k}\,|^2-|\,\mathbf{K}_n+\mathbf{k}\,|^2-\lambda-\lambda^3\zeta')^{-3}\right] \\
&=-\lambda^2\zeta'+\text{terms of higher order than second in }\lambda\ . \qquad \text{(A25)}
\end{aligned}
$$

This implies $\zeta'=0$ and, finally, for the eigenvalues $E_n(\mathbf{k})=|\mathbf{k}+\mathbf{K}_n|^2+\lambda$. It is conjectured that, similar to second- and third-order terms, fourth- and higher-order terms also lead to vanishing corrections for the eigenvalues. Because the investigation of higher orders is still more complicated than for the second and third orders, it was not done and the conjecture is based on the results of Ref. 17. There it was shown that the multiple-scattering equations used here converge to the exact results if possibly diverging angular-momentum expansions are summed by the Borel technique.

[1]J. Korringa, Physica **13**, 392 (1947).
[2]W. Kohn and N. Rostocker, Phys. Rev. **94**, 1111 (1954).
[3]A. Bansil, Phys. Rev. Lett. **41**, 1670 (1978).
[4]G. M. Stocks, W. M. Temmerman, and B. L. Gyorffy, Phys. Rev. Lett. **41**, 339 (1978).
[5]J. S. Faulkner, in *Progress in Materials Science,* edited by J. W. Christian, P. Haasen, and T. B. Massalski (Pergamon, Oxford, 1982), pp. 1–187.
[6]R. Zeller and P. H. Dederichs, Phys. Rev. Lett. **42**, 1713 (1979).
[7]P. J. Braspenning, R. Zeller, A. Lodder, and P. H. Dederichs, Phys. Rev. B **29**, 703 (1984).
[8]H. Bross and K. H. Anthony, Phys. Status Solidi **22**, 667 (1967).
[9]F. Beleznay and M. J. Lawrence, J. Phys. C **1**, 1288 (1968).
[10]A. R. Williams, Phys. Rev, B **1**, 3417 (1970).
[11]M. A. Ball, J. Phys. C **5**, L23 (1972).
[12]A. R. Williams and J. van W. Morgan, J. Phys. C **5**, L293 (1972).
[13]A. R. Williams and J. van W. Morgan, J. Phys. C **7**, 37 (1974).
[14]R. G. Brown and M. Ciftan, Phys. Rev. B **27**, 4564 (1983).
[15]A. Gonis, Phys. Rev. B **33**, 5914 (1986).
[16]C. R. Natoli, M. Benfatto, and S. Doniach, Phys. Rev. B **34**, 4682 (1986).
[17]R. Zeller, J. Phys. C **20**, 2347 (1987).
[18]E. Badralexe and A. J. Freeman, Phys. Rev. B **36**, 1378 (1987).
[19]P. Ziesche, J. Phys. C **7**, 1085 (1974).
[20]J. S. Faulkner, Phys. Rev. B **19**, 6186 (1979).
[21]R. G. Brown and M. Ciftan, Phys. Rev. B **32**, 1343 (1985).
[22]R. G. Brown and M. Ciftan, Phys. Rev. B **33**, 7937 (1986).
[23]J. S. Faulkner, Phys. Rev. B **32**, 1339 (1985).
[24]J. S. Faulkner, Phys. Rev. B **34**, 5931 (1986).
[25]See standard references for Fredholm theory or, e.g., H. Margenau and G. M. Murphy, *The Mathematics of Physics and Chemistry,* 2nd ed. (van Nostrand, Princeton, 1956), Vol. 1, pp. 526 and 527.
[26]M. Danos and L. C. Maximon, J. Math. Phys. **6**, 766 (1965).
[27]M. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions* (U. S. GPO, Washington, D. C., 1964), pp. 360 and 440.