PHYSICAL REVIEW B VOLUME 36, NUMBER 3 15 JULY 1987-II

T operators and their matrix elements for a general periodic potential

E. Badralexe and A. J. Freeman
Department of Physics and Astronomy, Northwestern University, Evanston, Illinois 60201

(Received 29 December 1986)

A new approach for the treatment of the T operator is provided which cures the difficulties of the multiple-scattering approach to the general (non-muffin-tin) periodic potential problem. Solely from potential periodicity, i.e., without discriminating between muffin-tin and non-muffin-tin cases, the T operators are shown to admit a direct integral decomposition in terms of the reduced T operators. This feature is further exploited by introducing "Bloch periodic scattering states" which finally results in a closed (compact) expression for the on-shell matrix elements. In the L representation, their functional form is related to that derived within multiple-scattering theory for the muffin-tin case but *irrespective* of whether the potential is muffin tin or not, the structure dependence cannot be separated from that of the potential (as known in the multiple-scattering approach for the muffin-tin case). However, this separation can be restored by introducing various approximations which partially break the Bloch periodicity. Hence, the separation between structure and potential, even in the muffin-tin case, is shown to be an approximate result.

I. INTRODUCTION

The rapid growth of experimental determinations of the electronic structure of both ordered and disordered solids, surfaces, and interfaces has brought into sharp focus the need for local-density energy-band methods which can provide solutions for these systems with general potentials. A particularly successful approach has recently been developed–the full-potential linearized augmented plane-wave (FLAPW) method[1]–which has been shown to provide precise solutions for a large class of problems. Its very success calls additional attention to a need for a similar development of an energy-band method based on finding the T matrix or the Green function for a general periodic potential. In doing this we face the question of either using multiple-scattering theory or inventing another, more convenient, theory.

As is well known, multiple-scattering theory has played an important role for ordered solids since the work of Korringa,[2] Kohn and Rostoker,[2] Beeby,[3] and that of Soven,[4] Stocks *et al.*,[5] and Faulkner and Stocks[6] in developing the KKR-coherent-potential approximation (KKR-CPA) for substitutional disordered materials. A crucial role in these methods is played by the imposition of the muffin-tin (MT) approximation to the (general) periodic potential. This imposition allows the use of the well-known decomposition of the Green function between two adjacent cells which, in turn, results in the exact separation of the lattice structure (expressed as the KKR structure constants) from the crystal potential. Specifically (see Appendix), the on-shell total T matrix for a MT periodic potential is described in terms of a structure constant and the on-shell T matrix for a single MT, which can be further described by means of the phase shifts produced by a single MT potential. The (rather striking) feature of this result raises the question of whether the appearance of the structure constant is characteristic of the MT approximation *or* is instead connected with the periodicity. More than that, one can ask if it is possible to describe a general (non-MT) periodic potential in a formalism similar to the variable-phase method[7,8] (which generalizes the phase-shift description to the nonspherical symmetric potential). Finally, one can ask for the expression, should it exist, of the total T matrix for a general (non-MT) periodic potential. (Alternatively, one can ask for the existence of a band-structure equation of the KKR type; obviously, this is less general than the existence of the T matrix.)

To the best of our knowledge, these questions have not yet been answered. A number of attempts have been reported, using multiple-scattering theory and the variational principle, among which we cite the most recent.[9,10,11] [References 9 and 10 claim to have derived exact results; Ref. 11 derives the (same) result given in Ref. 10 as an approximate result and also discusses the accuracy of this approximation.] As mentioned by Faulkner,[12] however, "This problem cannot be considered as solved because the algebraic arguments that have been advanced lead to contradictory conclusions." It has even been argued that the problem of the total T matrix for a non-MT periodic potential is not tractable, as the off-shell T matrix of the single cell is involved and the corresponding Born series can no longer be summed analytically.[13] Of course, a formal solution can be easily produced, as discussed by Lloyd and Smith,[14] by first solving for the interstitial contributions, and thus reducing the problem to the muffin-tin form. In this solution, the interstitial contribution already contains part of the structure, and therefore the relation between structure and potential is obscured.

Apart from multiple-scattering theory, Nesbet[15] developed recently a new line of investigation. By using a variational principle, an R-matrix formalism is established for an arbitrary unit cell; after introducing an approximation concerning the trial function [relation (2) in Ref. 15], the result is a KKR-type equation which essentially coincides with that presented as an exact result by Gonis,[10] and as an approximate result by Nagano and Tong.[11]

In a previous paper,[16] we have shown for the case of a general periodic potential that the eigenvalue equation of the Bloch function (which leads to the usual plane-wave diagonalization) can be converted into a KKR-type equation. Essentially, this was done by introducing a (Bloch periodic) prolongation of the Bloch function in a sphere with arbitrary large radius and finding its multipole expansion. Then, the Bloch function in the unit cell is obtained by a folding-back procedure which finally results in a KKR-type equation. Unlike the MT case, in this equation the structure is no longer separated from the potential; instead, a supplementary structure dependence appears, which reflects the folding procedure which, in turn, takes into account the periodicity. This equation reproduces, in the soluble case of a constant periodic potential, the correct band structure (as given by the plane-wave diagonalization). Finally, it was demonstrated that (i) the separation between structure and potential can be restored by introducing various approximations, and (ii) this separation becomes an exact result within the "generalized muffin-tin approximation" which assumes the potential is zero in a small vicinity near the cell boundary.[16]

Here we address the problem of the total T matrix for a general periodic potential without using the traditional tool of multiple-scattering theory, namely the on-shell decomposition of the Bloch periodic Green function between two adjacent cells.[2,3,9–11,13] Instead, we consider a general periodic potential, and derive from the periodicity alone (hence, without discriminating between MT and non-MT potentials) that the $[L^2(R^3)]$ kernel of the T operator can be expressed as an integral over the Brillouin zone of a reduced kernel which is defined in the Hilbert space of Bloch functions. Further, the reduced kernel can be analyzed in a formalism akin to that of the usual scattering theory,[17] i.e., one can define (Bloch periodic) "in" and "out" states which are related to the (Bloch periodic) free states by means of the on-shell T matrix. In finding these states we use the previous idea[16] of finding the multipole expansion of the (Bloch periodic) prolongation of a Bloch periodic function and subsequently finding the function by a folding-back procedure. Thus, the on-shell matrix elements of the total T operators are calculated and their poles are shown to generate the energy-band structure as given by a previously determined band equation[16] (shown, as stated, to be equivalent with the result of the plane-wave diagonalization). Finally, by introducing various approximations (which essentially break the Bloch periodicity), one can easily obtain previous results derived with multiple-scattering theory. In particular, it is worth mentioning that the separation of structure and potential, which is derived by multiple-scattering theory for the muffin-tin periodic potential is shown to be only an approximation (which partially violates the Bloch boundary conditions) and hence is not, as long believed,[2] an exact result.

II. $T^{\pm}(E)$ OPERATORS AND THEIR KERNELS

Let $\mathbf{R},\mathbf{K}\in Z^3$ be vectors of the direct and reciprocal lattices, having the primitive cells Ω and $\tilde{\Omega}$, with the volumes ω and $\tilde{\omega}$, respectively. $[\mathbf{R}\cdot\mathbf{K}=2\pi\times\text{integer}, \omega\tilde{\omega}=(2\pi)^3]$. Let $\boldsymbol{\rho}\in\Omega$ and $\boldsymbol{\kappa}\in\tilde{\Omega}$ be vectors in the direct and reciprocal primitive cell, respectively. Then, for any vectors $\mathbf{r},\mathbf{k}$ in the whole space R^3, there is a unique decomposition

$$\begin{aligned} \mathbf{r}&=\mathbf{R}+\boldsymbol{\rho}\ ,\\ \mathbf{k}&=\mathbf{K}+\boldsymbol{\kappa}\ . \end{aligned} \tag{1}$$

Let $V(\mathbf{r})$, $\mathbf{r}\in R^3$, be a periodic potential over N_Ω cells in the crystal with $N_\Omega\to\infty$, as given by a sum of cell potentials

$$V=\sum_{\mathbf{R}}\mathcal{V}_{\mathbf{R}}\ , \tag{2}$$

where

$$\mathcal{V}_{\mathbf{R}}(\mathbf{r})=\begin{cases}0 & \text{for } \mathbf{r}\neq\mathbf{R}+\boldsymbol{\rho}\\ \mathcal{V}(\boldsymbol{\rho}) & \text{for } \mathbf{r}=\mathbf{R}+\boldsymbol{\rho},\end{cases} \tag{3a}$$

and the function $\mathcal{V}(\boldsymbol{\rho})$ (which has an arbitrary range α, $\alpha\leq\max_{\rho\in\Omega}\rho$) defines the potential (in the whole space)

$$\mathcal{V}(\mathbf{r})=\begin{cases}0 & \text{otherwise}\\ \mathcal{V}(\boldsymbol{\rho}) & \text{for } \mathbf{r}\in\Omega.\end{cases} \tag{3b}$$

In this notation, the muffin-tin case is obtained for $\alpha=\mu$, where μ denotes the radius of the inscribed sphere in the unit cell Ω. Finally, for any finite d, $d\geq0$, we introduce the potential $V^d(\mathbf{r})$, as defined by

$$V^d(\mathbf{r})=\begin{cases}V(\mathbf{r}) & \text{for } r\leq d\\ 0 & \text{otherwise,}\end{cases} \tag{4}$$

where $V(\mathbf{r})$ is defined in Eq. (2). Obviously, V^μ denotes the muffin-tin part of the cell potential $\mathcal{V}$.

Assume that the equation of the $T^{\pm}(E)$ operators is given by

$$T^{\pm}(E)=V+VG_0^{\pm}(E)T^{\pm}(E)\ , \tag{5}$$

where the potential V was defined in Eq. (2) and the kernel of the Green function is given by[18]

$$\begin{aligned} G_0^{\pm}(E,\mathbf{r},\mathbf{r}')&=\frac{-1}{4\pi}\frac{e^{\pm i\sqrt{E}\,|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|}\\ &=\frac{\mp i\pi\sqrt{E}}{2}\sum_L j_L(E,\mathbf{r}_<)h_L^{\mp *}(E,\mathbf{r}_>)\ , \end{aligned} \tag{6}$$

where $L=(l,m)$ and, as usual, the Bessel (j_L), Neumann (n_L), the Hankel functions $h_L^{\pm}(E,\mathbf{r})=j_L(E,\mathbf{r})\pm in_L(E,\mathbf{r})$ are products of the spherical Bessel, Neumann, and Hankel functions and spherical harmonics.

We first want to find the way in which the operators $T^{\pm}(E)$ defined by Eq. (5) reflect the periodicity of the potential V defined in Eq. (2). We suppose, for the moment, that the potential is weak enough so that Eq. (5) admits a perturbative series expansion, and write it in the coordinate representation

$$T^{\pm}(E,\mathbf{R}+\boldsymbol{\rho},\mathbf{R}'+\boldsymbol{\rho}')=\mathcal{V}(\boldsymbol{\rho})\delta(\boldsymbol{\rho}-\boldsymbol{\rho}')\delta_{\mathbf{RR}'}+\mathcal{V}(\boldsymbol{\rho})G_0^{\pm}(E,\boldsymbol{\rho},\mathbf{R}'-\mathbf{R}+\boldsymbol{\rho}')\mathcal{V}(\boldsymbol{\rho}')$$
$$+\mathcal{V}(\boldsymbol{\rho})\int_{\Omega}\sum_{\mathbf{R}''}G_0^{\pm}(E,\boldsymbol{\rho},\mathbf{R}''-\mathbf{R}+\boldsymbol{\rho}'')\mathcal{V}(\boldsymbol{\rho}'')G_0^{\pm}(E,\boldsymbol{\rho}'',\mathbf{R}'-\mathbf{R}''+\boldsymbol{\rho}')d\boldsymbol{\rho}''\mathcal{V}(\boldsymbol{\rho}')+\cdots\ , \tag{7}$$

where use was made of Eqs. (1) and (3).

It is then advantageous to use the relation[19]

$$\int_{\tilde{\Omega}}\frac{d\boldsymbol{\kappa}}{\tilde{\omega}}e^{i\boldsymbol{\kappa}\cdot(\mathbf{R}-\mathbf{R}')}=\delta_{\mathbf{RR}'} \tag{8}$$

and to introduce the (Bloch periodic) Green function $\mathcal{G}_0^{\pm}(\boldsymbol{\kappa},E)$ whose kernel (in the Hilbert space of Bloch periodic functions[17]) is given by[2,17]

$$\mathcal{G}_0^{\pm}(\boldsymbol{\kappa},E,\boldsymbol{\rho},\boldsymbol{\rho}')=\sum_{\mathbf{R}}e^{i\boldsymbol{\kappa}\cdot\mathbf{R}}\frac{-1}{4\pi}\frac{e^{\pm\sqrt{E}\,|\boldsymbol{\rho}-\mathbf{R}-\boldsymbol{\rho}'|}}{|\boldsymbol{\rho}-\mathbf{R}-\boldsymbol{\rho}'|}$$
$$=\frac{1}{\omega}\sum_{\mathbf{K}}\frac{e^{i(\boldsymbol{\kappa}+\mathbf{K})(\boldsymbol{\rho}-\boldsymbol{\rho}')}}{E\pm i\epsilon-(\boldsymbol{\kappa}+\mathbf{K})^2}\ . \tag{9}$$

By using Eqs. (9) and (8), Eq. (7) becomes

$$T^{\pm}(E,\mathbf{R}+\boldsymbol{\rho},\mathbf{R}'+\boldsymbol{\rho}')=\int_{\tilde{\Omega}}\frac{d\boldsymbol{\kappa}}{\tilde{\omega}}e^{i\boldsymbol{\kappa}\cdot(\mathbf{R}-\mathbf{R}')}\mathcal{T}^{\pm}(\boldsymbol{\kappa},E,\boldsymbol{\rho},\boldsymbol{\rho}'), \tag{10}$$

where we introduced the kernel $\mathcal{T}^{\pm}(\boldsymbol{\kappa},E,\boldsymbol{\rho},\boldsymbol{\rho}')$ as defined by

$$\mathcal{T}^{\pm}(\boldsymbol{\kappa},E,\boldsymbol{\rho},\boldsymbol{\rho}')$$
$$=\mathcal{V}(\boldsymbol{\rho})\delta(\boldsymbol{\rho}-\boldsymbol{\rho}')+\mathcal{V}(\boldsymbol{\rho})\mathcal{G}_0^{\pm}(\boldsymbol{\kappa},E,\boldsymbol{\rho},\boldsymbol{\rho}')\mathcal{V}(\boldsymbol{\rho}')$$
$$+\mathcal{V}(\boldsymbol{\rho})\int_{\Omega}\mathcal{G}_0^{\pm}(\boldsymbol{\kappa},E,\boldsymbol{\rho},\boldsymbol{\rho}'')\mathcal{V}(\boldsymbol{\rho}'')$$
$$\times\mathcal{G}_0^{\pm}(\boldsymbol{\kappa},E,\boldsymbol{\rho}'',\boldsymbol{\rho}')d\boldsymbol{\rho}''\mathcal{V}(\boldsymbol{\rho}')+\cdots\ . \tag{11}$$

Alternatively, the kernel $\mathcal{T}^{\pm}(\boldsymbol{\kappa},E,\boldsymbol{\rho},\boldsymbol{\rho}')$ can be thought of as the solution of

$$\mathcal{T}^{\pm}(\boldsymbol{\kappa},E,\boldsymbol{\rho},\boldsymbol{\rho}')=\mathcal{V}(\boldsymbol{\rho})\delta(\boldsymbol{\rho}-\boldsymbol{\rho}')$$
$$+\mathcal{V}(\boldsymbol{\rho})\int_{\Omega}\mathcal{G}_0^{\pm}(\boldsymbol{\kappa},E,\boldsymbol{\rho},\boldsymbol{\rho}'')$$
$$\times\mathcal{T}^{\pm}(\boldsymbol{\kappa},E,\boldsymbol{\rho}'',\boldsymbol{\rho}')d\boldsymbol{\rho}''\ , \tag{12}$$

and, in turn, defines an operator $\mathcal{T}^{\pm}(\boldsymbol{\kappa},E)$ (in the Hilbert space of Bloch periodic functions) which is given by

$$\mathcal{T}^{\pm}(\boldsymbol{\kappa},E)=\mathcal{V}+\mathcal{V}\mathcal{G}_0^{\pm}(\boldsymbol{\kappa},E)\mathcal{T}^{\pm}(\boldsymbol{\kappa},E)\ . \tag{13}$$

So far, we have shown that the $T^{\pm}$ operators defined in Eq. (5) by a perturbative (weak enough) periodic potential has a particular structure as given by Eqs. (10) and (13), where the operators $\mathcal{T}^{\pm}(\boldsymbol{\kappa},E)$ can be called the reduced $T^{\pm}$ operators. In fact, Eqs. (10) and (13) assert the existence of the lattice Fourier transform

$$\mathcal{T}^{\pm}(\boldsymbol{\kappa},E,\boldsymbol{\rho},\boldsymbol{\rho}')=\sum_{\mathbf{R}-\mathbf{R}'}e^{-i\boldsymbol{\kappa}\cdot(\mathbf{R}-\mathbf{R}')}T^{\pm}(E,\mathbf{R}+\boldsymbol{\rho},\mathbf{R}'+\boldsymbol{\rho}')\ , \tag{14}$$

or, in other words, the left-hand side (lhs) of Eq. (7) depends not on $\mathbf{R}$ and $\mathbf{R}'$ but only on $\mathbf{R}-\mathbf{R}'$.[20]

We now want to extend these results for the case of a general periodic potential. To do this, we define the total Green function

$$G^{\pm}(E)=G_0^{\pm}(E)+G_0^{\pm}(E)VG^{\pm}(E) \tag{15a}$$

which apparently satisfies the relation

$$T^{\pm}(E)=V+VG^{\pm}(E)V \tag{15b}$$

and can be shown to satisfy, for a perturbative periodic potential, relations similar to Eqs. (6)–(13),

$$G^{\pm}(E,\mathbf{R}+\boldsymbol{\rho},\mathbf{R}'+\boldsymbol{\rho}')=\int_{\tilde{\Omega}}\frac{d\boldsymbol{\kappa}}{\tilde{\omega}}e^{i\boldsymbol{\kappa}\cdot(\mathbf{R}-\mathbf{R}')}\mathcal{G}^{\pm}(\boldsymbol{\kappa},E,\boldsymbol{\rho},\boldsymbol{\rho}')\ ,$$
$$\mathcal{G}^{\pm}(\boldsymbol{\kappa},E)=\mathcal{G}_0^{\pm}(\boldsymbol{\kappa},E)+\mathcal{G}_0^{\pm}(\boldsymbol{\kappa},E)\mathcal{V}\mathcal{G}^{\pm}(\boldsymbol{\kappa},E)\ . \tag{16}$$

Now, suppose that the potential V is no longer a perturbation, but can be written as a sum

$$V=V_1+V_2\ ,$$
$$\mathcal{V}=\mathcal{V}_1+\mathcal{V}_2\ , \tag{17}$$

where V_2 or $\mathcal{V}_2$ represents a perturbation to the potential V_1 or $\mathcal{V}_1$, respectively. Then, Eq. (15a) can be written in the form

$$G^{\pm}(E)=G_1^{\pm}(E)+G_1^{\pm}(E)V_2G^{\pm}(E)\ , \tag{18}$$

where the Green function $G_1^{\pm}(E)$ takes into account only the potential V_1. Further, by repeating the analysis given in Eqs. (6)–(13), and by using Eq. (15b), we see that the Fourier transform, Eq. (14), exists irrespective of whether the potential is perturbative or not. Then, by taking the lattice Fourier transform of Eq. (5), we conclude that the decomposition, Eqs. (10) and (13), holds irrespective of whether the potential is perturbative or not. Obviously, in the last case, the series in Eq. (11) is no longer convergent, and therefore Eq. (13) should be solved by means other than the Born series.

Thus, we have shown that the study of the $T^{\pm}(E)$ operators defined by Eq. (5) [in $L^2(R^3)$] can be simplified to the study of the reduced $\mathcal{T}^{\pm}(\boldsymbol{\kappa},E)$ operators defined by Eq. (13) (in the Hilbert space of Bloch functions). [Compare also Eq. (13) with Eq. (A3) in Appendix A of the usual scattering theory for a finite range potential.] If we now introduce the Hilbert space $\mathcal{H}(\boldsymbol{\kappa})$ spanned by the plane waves $(e^{i(\boldsymbol{\kappa}+\mathbf{K})\cdot\boldsymbol{\rho}}/\sqrt{\omega})_{\mathbf{K}}$, and the Hilbert space $\mathcal{H}$ as defined by the (continual) direct sum[17]

$$\mathcal{H}=\int_{\tilde{\Omega}}^{\oplus}\frac{d\boldsymbol{\kappa}}{\tilde{\omega}}\mathcal{H}(\boldsymbol{\kappa}) \tag{19}$$

then we learn from Eqs. (10) and (13) that the $T^{\pm}(E)$ operators defined in Eq. (5) admit a continual direct-sum decomposition. Such a decomposition was exhaustively discussed by Reed and Simmon[17] for the case of the Bloch periodic Hamiltonian, and in fact, was known long ago[3] but in a primitive form concerning only the on-shell matrix elements (i.e., only for the on-shell component of the T operators) and only in the muffin-tin case. Recently, this type of decomposition was used for asymptotic expansions (at high energy) and for the soluble case of the Kronnig-Penney model.[21] It follows then, that the novelty of the continual direct sum, Eqs. (10) and (13), consists in having been proven for a general potential and for the kernel $T^{\pm}(E,\mathbf{r},\mathbf{r}')$, which contains both the on- and off-shell components. Hereafter, we avoid the discussion of general properties of such a decomposition in the favor of explicit, clear-cut constructions. Hence, in the next section, we calculate the matrix elements of the operators defined in Eq. (5).

III. MATRIX ELEMENTS

We are interested in calculating the on-shell matrix elements[22]

$$T^{\pm}_{LL'}(E)=\int_{R^3}\int_{R^3} j^*_L(E,\mathbf{r})T^{\pm}(E,\mathbf{r},\mathbf{r}')\times j_{L'}(E,\mathbf{r}')d\mathbf{r}\,d\mathbf{r}' \ . \tag{20}$$

For the sake of completeness, we also calculate the plane-wave matrix elements

$$T^{\pm}_{\hat{\mathbf{p}}\hat{\mathbf{p}}'}(E)=\int_{R^3}\int_{R^3}\frac{e^{-i\sqrt{E}\hat{\mathbf{p}}\cdot\mathbf{r}}}{(2\pi)^{3/2}}T^{\pm}(E,\mathbf{r},\mathbf{r}')\times\frac{e^{i\sqrt{E}\hat{\mathbf{p}}\cdot\mathbf{r}'}}{(2\pi)^{3/2}}d\mathbf{r}\,d\mathbf{r}' \ . \tag{21}$$

By using Eq. (10), the matrix elements given in Eqs. (20) and (21) become

$$T^{\pm}_{LL'}(E)=\int_{\tilde{\Omega}}\frac{d\boldsymbol{\kappa}}{\tilde{\omega}}\mathcal{T}^{\pm}_{LL'}(\boldsymbol{\kappa},E) \tag{22a}$$

and

$$T^{\pm}_{\hat{\mathbf{p}}\hat{\mathbf{p}}'}(E)=\int_{\tilde{\Omega}}\frac{d\boldsymbol{\kappa}}{\tilde{\omega}}\mathcal{T}^{\pm}_{\hat{\mathbf{p}}\hat{\mathbf{p}}'}(\boldsymbol{\kappa},E) \ , \tag{22b}$$

where we introduced the matrix elements of the reduced operators

$$\mathcal{T}^{\pm}_{\lambda\lambda'}(\boldsymbol{\kappa},E)=\int_{\Omega}\int_{\Omega}\Psi^*_{0_\lambda}(\boldsymbol{\kappa},E,\boldsymbol{\rho})\mathcal{T}^{\pm}(\boldsymbol{\kappa},E,\boldsymbol{\rho},\boldsymbol{\rho}')\times\Psi_{0_{\lambda'}}(\boldsymbol{\kappa},E,\boldsymbol{\rho}')d\boldsymbol{\rho}\,d\boldsymbol{\rho}' \ , \tag{23}$$

where λ stands for either L or $\hat{\mathbf{p}}$, and the (Bloch periodic) functions $\Psi_{0\lambda}(\boldsymbol{\kappa},E,\boldsymbol{\rho})$ are given by

$$\Psi_{0_L}(\boldsymbol{\kappa},E,\boldsymbol{\rho})=j_L(\boldsymbol{\kappa},E,\boldsymbol{\rho})=\sum_{\mathbf{R}}e^{-i\boldsymbol{\kappa}\cdot\mathbf{R}}j_L(E,\mathbf{R}+\boldsymbol{\rho}) \ , \tag{24}$$

$$\Psi_{0_{\hat{\mathbf{p}}}}(\boldsymbol{\kappa},E,\boldsymbol{\rho})=\sum_{\mathbf{R}}e^{-i\boldsymbol{\kappa}\cdot\mathbf{R}}\frac{e^{i\sqrt{E}\hat{\mathbf{p}}(\mathbf{R}+\boldsymbol{\rho})}}{(2\pi)^{3/2}} \ . \tag{25}$$

At this point it is necessary to pause and to obtain more insight into the folding procedure used in Eqs. (24) and (25). For this, we recall the relations[19]

$$\begin{gathered}\sum_{\mathbf{R}}e^{i\boldsymbol{\kappa}\cdot\mathbf{R}}=\tilde{\omega}\sum_{\mathbf{K}}\delta(\mathbf{k}-\mathbf{K}) \ , \\ \lim_{N_\Omega\to\infty}\frac{1}{N_\Omega}\sum_{\mathbf{R}}e^{-i\mathbf{k}\cdot\mathbf{R}}=\begin{cases}1 & \text{if } \mathbf{k}=\mathbf{K}\\ 0 & \text{otherwise.}\end{cases}\end{gathered} \tag{26}$$

The meaning of Eq. (25) is then quite obvious; the function $\Psi_{0_{\hat{\mathbf{p}}}}(\boldsymbol{\kappa},E,\boldsymbol{\rho})$ can also be written in the form

$$\Psi_{0_{\hat{\mathbf{p}}}}(\boldsymbol{\kappa},E,\boldsymbol{\rho})=\tilde{\omega}^{1/2}\sum_{\mathbf{K}}\frac{e^{i(\boldsymbol{\kappa}+\mathbf{K})\cdot\boldsymbol{\rho}}}{\sqrt{\omega}}\delta(\sqrt{E}\hat{\mathbf{p}}-\boldsymbol{\kappa}-\mathbf{K}) \ , \tag{27}$$

that is, the function $\Psi_{0_{\hat{\mathbf{p}}}}(\boldsymbol{\kappa},E,\boldsymbol{\rho})$ is a superposition in the space $\mathcal{H}(\boldsymbol{\kappa})$, and the coefficients are not numbers but rather distributions. In fact, since from Eqs. (25) and (8) we have the relation[17]

$$\int_{\tilde{\Omega}}\frac{d\boldsymbol{\kappa}}{\tilde{\omega}}\int_{\Omega}\Psi^*_{0_{\hat{\mathbf{p}}}}(\boldsymbol{\kappa},E,\boldsymbol{\rho})\Psi_{0_{\hat{\mathbf{p}}'}}(\boldsymbol{\kappa},E',\boldsymbol{\rho}')d\boldsymbol{\rho}=\frac{\delta(\sqrt{E}-\sqrt{E}\,')}{E}\delta(\hat{\mathbf{p}}-\hat{\mathbf{p}}') \ , \tag{28}$$

it follows that the function $\Psi_{0_{\hat{\mathbf{p}}}}(\boldsymbol{\kappa},E,\boldsymbol{\rho})$ is a generalized element (i.e., normalized to a δ function) of the Hilbert space $\mathcal{H}$ defined in Eq. (19). The translation properties of the function in Eq. (24) are given by[23]

$$\begin{aligned}j_L(E,\mathbf{r}+\mathbf{r}')&=\sum_{L'}j_{L'}(E,\mathbf{r})J_{L'L}(E,\mathbf{r}')\\&=\sum_{L'}j_{L'}(E,\mathbf{r}')J_{L'L}(E,\mathbf{r}) \ ,\end{aligned} \tag{29}$$

where

$$\begin{gathered}J_{L'L}(E,\mathbf{r})=\sum_{L''}I_{L'L''}j_{L''}(E,\mathbf{r}) \ , \\ I^L_{L'L''}=(2\pi)^{3/2}i^{l'+l''-l}\int_{4\pi}Y^*_{L'}(\hat{\mathbf{r}})Y^*_{L''}(\hat{\mathbf{r}})Y_L(\hat{\mathbf{r}})d\hat{\mathbf{r}} \ ,\end{gathered} \tag{30}$$

and the sum in Eq. (29) converges irrespective of the ratio of the modulus r and r'.

A number of properties are almost evident from Eq. (30)

$$J_{L'L}(E,0)=\delta_{L'L} \ , \tag{31a}$$

$$\sum_{L''}J_{L'L''}(E,\mathbf{r}')J_{L''L}(E,\mathbf{r})=J_{L'L}(E,\mathbf{r}+\mathbf{r}') \ , \tag{31b}$$

$$J^*_{L'L}(E,\mathbf{r})=J_{LL'}(E,-\mathbf{r}) \ . \tag{31c}$$

Further, it is advantageous to introduce the matrix

$$J_{L'L}(\boldsymbol{\kappa},E)=\sum_{\mathbf{R}}e^{-i\boldsymbol{\kappa}\cdot\mathbf{R}}J_{L'L}(E,\mathbf{R}) \ , \tag{32}$$

which, after some algebra becomes

$$J_{L'L}(\boldsymbol{\kappa},E)=\tilde{\omega}i^{l'-l}\sum_{\mathbf{K}}Y^*_{L'}(\hat{\mathcal{K}})\frac{\delta(\sqrt{E}-[(\boldsymbol{\kappa}+\mathbf{K})^2]^{1/2})}{E}\times Y_L(\hat{\mathcal{K}}) \ , \tag{33}$$

where $\mathcal{K}=\boldsymbol{\kappa}+\mathbf{K}$ and $J_{L'L}(\boldsymbol{\kappa},E)$ has the obvious properties

$$\int_{\tilde{\Omega}}\frac{d\boldsymbol{\kappa}}{\tilde{\omega}}e^{i\boldsymbol{\kappa}\cdot\mathbf{R}}J_{L'L}(\boldsymbol{\kappa},E)=J_{L'L}(E,\mathbf{R}) \ , \tag{34a}$$

$$\sum_{L'}J_{L''L'}(\boldsymbol{\kappa},E)J_{L'L}(\boldsymbol{\kappa},E)=J_{L''L}(\boldsymbol{\kappa},E)N_\Omega \ , \tag{34b}$$

$$J_{L'L}(\boldsymbol{\kappa},E)=J^*_{LL'}(\boldsymbol{\kappa},E) \ , \tag{34c}$$

where, again, $N_\Omega\to\infty$ stands for the number of the unit cells and $\mathbf{R}$ denotes lattice vectors. It follows then that the function defined in Eq. (24) can be written in the form

$$\Psi_{0_L}(\boldsymbol{\kappa},E,\boldsymbol{\rho})=j_L(\boldsymbol{\kappa},E,\boldsymbol{\rho})=\sum_{L'}j_{L'}(E,\boldsymbol{\rho})J_{L'L}(E,\boldsymbol{\kappa})$$

$$=\tilde{\omega}^{1/2}i^{-l}\sum_{\mathbf{K}}\frac{e^{i(\boldsymbol{\kappa}+\mathbf{K})\rho}}{\sqrt{\omega}}\frac{\delta(\sqrt{E}-[(\kappa+K)^2]^{1/2})}{E}Y_L(\mathcal{K})\ , \tag{35a}$$

$$\Psi^*_{0_L}(\boldsymbol{\kappa},E,\boldsymbol{\rho})=\sum_{L'}J_{LL'}(E,\boldsymbol{\kappa})j^*_{L'}(E,\boldsymbol{\rho})\ . \tag{35b}$$

Then, similarly to the case of the function $\Psi_{0_{\hat{\mathbf{p}}}}(\boldsymbol{\kappa},E,\boldsymbol{\rho})$, we conclude that the function $\Psi_{0_L}(\boldsymbol{\kappa},E,\boldsymbol{\rho})$ is a superposition in the space $\mathcal{H}(\boldsymbol{\kappa})$ where the coefficients are not numbers, but distributions. Also, since we have the relation [obtained from Eqs. (8) and (24)]

$$\int_{\tilde{\Omega}}\frac{d\boldsymbol{\kappa}}{\tilde{\omega}}\Psi^*_{0_L}(\boldsymbol{\kappa},E,\boldsymbol{\rho})\Psi_{0_{L'}}(\boldsymbol{\kappa},E,\boldsymbol{\rho})d\boldsymbol{\rho}=\frac{\delta(\sqrt{E}-\sqrt{E'})}{E}\delta_{LL'}\ , \tag{36}$$

it follows that the function $\Psi_{0_L}(\boldsymbol{\kappa},E,\boldsymbol{\rho})$ belong to the space $\mathcal{H}$ defined in Eq. (19).

Now since we have seen the meaning of the functions in Eqs. (24) and (25),[24] we come back to the *T* matrix and calculate the matrix elements given in Eq. (23) and hence, by means of Eq. (22), the matrix elements defined by Eqs. (20) and (21). Thus, we introduce the functions $\Psi^{\pm}_{L}(\boldsymbol{\kappa},E,\boldsymbol{\rho})$ and $\Psi^{\pm}_{\hat{\mathbf{p}}}(\boldsymbol{\kappa},E,\boldsymbol{\rho})$

$$\Psi^{\pm}_{\lambda}(\boldsymbol{\kappa},E,\boldsymbol{\rho})=\Psi_{0_\lambda}(\boldsymbol{\kappa},E,\boldsymbol{\rho})+\int_{\Omega}\mathcal{G}^{\pm}_{0}(\boldsymbol{\kappa},E,\boldsymbol{\rho},\boldsymbol{\rho}')\mathcal{V}(\boldsymbol{\rho}')\times\Psi^{\pm}_{\lambda}(\boldsymbol{\kappa},E,\boldsymbol{\rho}')d\boldsymbol{\rho}' \tag{37}$$

(where, again, λ stands for either L or $\hat{\mathbf{p}}$). Notice that if we drop the inhomogeneous term in Eq. (37), we get the eigenvalue equation for the Bloch functions. Then, we can already see (by using the Fredholm alternative) that Eq. (37) has a solution whenever $E\neq E_n(\boldsymbol{\kappa})$, $n=1,2,\dots$, where $E_n(\boldsymbol{\kappa})$ are the discrete levels for a given $\boldsymbol{\kappa}\in\tilde{\Omega}$. Obviously, the functions $\Psi^{\pm}_{\lambda}(\boldsymbol{\kappa},E,\boldsymbol{\rho})$ have a distributional character [because of Eqs. (27) and (35)]; however, this is not too troublesome since we are interested in evaluating only integrals of these functions (and not their point by point values). Because of its similarity to the Lippman-Schwinger equation used in the ordinary scattering theory, Eq. (A15), we can call Eq. (37) the Bloch-periodic Lippman-Schwinger equation; accordingly, we can call the functions $\Psi^{\pm}_{\lambda}(\boldsymbol{\kappa},E,\boldsymbol{\rho})$ the Bloch periodic in and out states. However, their existence is only connected with a Dyson-type equation and they do not have the meaning of asymptotic free states (as in the case of usual scattering theory[17]).

In terms of the functions given in Eq. (37), the matrix elements (Eq. 23) which follow from Eqs. (13) and (37) are

$$\mathcal{T}^{\pm}_{\lambda\lambda'}(\boldsymbol{\kappa},E)=\int_{\Omega}\Psi^*_{0_\lambda}(\boldsymbol{\kappa},E,\boldsymbol{\rho})\mathcal{V}(\boldsymbol{\rho})\Psi^{\pm}_{\lambda'}(\boldsymbol{\kappa},E,\boldsymbol{\rho})d\boldsymbol{\rho} \tag{38}$$

[compare with Eq. (A14) of the usual scattering theory]. Thus, in order to find the matrix elements $\mathcal{T}^{\pm}_{\lambda\lambda'}(\boldsymbol{\kappa},E)$ [and hence, by means of Eq. (22), the matrix elements $T^{\pm}_{\lambda\lambda'}(E)$] we need the solution of Eq. (37), akin to ordinary scattering theory.[17] Therefore, we now focus on solving this equation.

A. Plane-wave representation

We begin with the (easier) plane-wave case $\lambda=\hat{\mathbf{p}}$, in which case Eq. (37) becomes [from Eqs. (9) and (27)]

$$\Psi^{\pm}_{\hat{\mathbf{p}}}(\boldsymbol{\kappa},E,\boldsymbol{\rho})=\sum_{\mathbf{K}}\frac{e^{i(\boldsymbol{\kappa}+\mathbf{K})\cdot\rho}}{\sqrt{\omega}}\left[\tilde{\omega}^{1/2}\delta(\sqrt{E}\,\hat{\mathbf{p}}-\boldsymbol{\kappa}-\mathbf{K})+\frac{1}{E\pm i\epsilon-(\boldsymbol{\kappa}+\mathbf{K})^2}\int_{\Omega}\frac{e^{i(\boldsymbol{\kappa}+\mathbf{K})\cdot\rho'}}{\sqrt{\omega}}\mathcal{V}(\boldsymbol{\rho}')\Psi^{\pm}_{\hat{\mathbf{p}}}(\boldsymbol{\kappa},E,\boldsymbol{\rho}')d\boldsymbol{\rho}'\right]\ . \tag{39}$$

Thus, the solution $\Psi^{\pm}_{\hat{\mathbf{p}}}(\boldsymbol{\kappa},E,\boldsymbol{\rho})$ takes the form

$$\Psi^{\pm}_{\hat{\mathbf{p}}}(\boldsymbol{\kappa},E,\boldsymbol{\rho})=\sum_{\mathbf{K}}\frac{e^{i(\boldsymbol{\kappa}+\mathbf{K})\cdot\rho}}{\sqrt{\omega}}a^{\pm}_{\mathbf{K}}(\boldsymbol{\kappa},E)\ , \tag{40}$$

which, by insertion into Eq. (39), results in the algebraic system for the coefficients

$$\sum_{\mathbf{K}'}\left[\delta_{\mathbf{K}\mathbf{K}'}-\frac{\mathcal{V}_{\mathbf{K}\mathbf{K}'}}{E\pm i\epsilon-(\boldsymbol{\kappa}+\mathbf{K})^2}\right]a^{\pm}_{\mathbf{K}'}(\boldsymbol{\kappa},E)=\tilde{\omega}^{1/2}\delta(\sqrt{E}\,\hat{\mathbf{p}}-\boldsymbol{\kappa}-\mathbf{K})\ , \tag{41}$$

where we introduced the notation

$$\mathcal{V}_{\mathbf{K}\mathbf{K}'}=\int_{\Omega}\frac{e^{-i(\boldsymbol{\kappa}+\mathbf{K})\cdot\rho}}{\sqrt{\omega}}\mathcal{V}(\boldsymbol{\rho})\frac{e^{i(\boldsymbol{\kappa}+\mathbf{K}')\cdot\rho}}{\sqrt{\omega}}d\rho\ . \tag{42}$$

Thus, providing $E\neq E_n(\boldsymbol{\kappa})$, the discrete levels for a fixed $\boldsymbol{\kappa}\in\tilde{\Omega}$, the coefficients $a^{\pm}_{\mathbf{K}}(\boldsymbol{\kappa},E)$ can be found by taking the inverse of the matrix in the lhs of Eq. (41). By using these results in Eq. (38) we obtain the matrix elements

$$\mathcal{T}^{\pm}_{\hat{\mathbf{p}}\hat{\mathbf{p}}'}(\boldsymbol{\kappa},E)=\tilde{\omega}\sum_{\mathbf{K},\mathbf{K}'}\delta(\sqrt{E}\,\hat{\mathbf{p}}-\boldsymbol{\kappa}-\mathbf{K})\mathfrak{T}^{\pm}_{\mathbf{K}\mathbf{K}'}(\boldsymbol{\kappa},E)\times\delta(\sqrt{E}\,\hat{\mathbf{p}}'-\boldsymbol{\kappa}-\mathbf{K}')\ , \tag{43}$$

where $\mathfrak{T}^{\pm}_{\mathbf{K}\mathbf{K}'}(\boldsymbol{\kappa},E)$ denotes the matrix

$$\mathfrak{T}^{\pm}_{\mathbf{K}\mathbf{K}'}(\boldsymbol{\kappa},E)=\sum_{\mathbf{K}''}\mathcal{V}_{\mathbf{K}\mathbf{K}''}\left[\delta_{\mathbf{K}''\mathbf{K}'}-\frac{\mathcal{V}_{\mathbf{K}''\mathbf{K}'}}{E\pm i\epsilon(\boldsymbol{\kappa}+\mathbf{K}'')^2}\right]^{-1} . \tag{44}$$

Equations (43) and (44) give the on-shell matrix elements in the plane-wave representation; it is easy to see, by using the **K** expansion from Eq. (9), that the off-shell matrix elements can be calculated in a similar way. Thus, the kernel $T^{\pm}(E,\mathbf{r},\mathbf{r}')$ of the operator defined in Eqs. (5), (10), and (13) is given by

$$T^{\pm}(E,\mathbf{r},\mathbf{r}')=\int_{\tilde{\Omega}}\frac{d\boldsymbol{\kappa}}{\tilde{\omega}}\sum_{\mathbf{K},\mathbf{K}'}\frac{e^{i(\boldsymbol{\kappa}+\mathbf{K})\cdot\mathbf{r}}}{\sqrt{\omega}}\mathfrak{T}^{\pm}_{\mathbf{K}\mathbf{K}'}(\boldsymbol{\kappa},E)\times\frac{e^{-i(\boldsymbol{\kappa}+\mathbf{K}')\cdot\mathbf{r}'}}{\sqrt{\omega}} . \tag{45}$$

Apparently, from Eqs. (43) and (44), the poles of the total operator coincide with those of its on-shell part and are given by the usual band-structure equation (which leads to the plane-wave diagonalization).

B. Angular momentum representation

We now turn to the case $\lambda=L$. Here we have to solve the equation

$$\Psi^{\pm}_{L}(\boldsymbol{\kappa},E,\boldsymbol{\rho})=\Psi_{0_L}(\boldsymbol{\kappa},E,\boldsymbol{\rho})+\int_{\Omega}\mathcal{G}^{\pm}_{0}(\boldsymbol{\kappa},E,\boldsymbol{\rho},\boldsymbol{\rho}')\mathcal{V}(\boldsymbol{\rho}')\times\Psi^{\pm}_{L}(\boldsymbol{\kappa},E,\boldsymbol{\rho}')d\boldsymbol{\rho}' \tag{46}$$

[compare with Eq. (A15) of the usual scattering theory]. Obviously, by using the **K** expansion given in Eqs. (9) and (35), one can express the corresponding matrix elements in terms of the matrix $\mathfrak{T}^{\pm}_{\mathbf{K}\mathbf{K}'}$ defined in Eq. (44).[25] However, an alternative, more interesting solution is made possible by the use of the L expansion in Eq. (35). Actually, from Eqs. (6), (9), and (35), the lhs of Eq. (46) takes the form

$$\Psi^{\pm}_{L}(\boldsymbol{\kappa},E,\boldsymbol{\rho})=\sum_{L'}Y_{L'}(\hat{\rho})X^{\pm}_{L'L}(\boldsymbol{\kappa},E,\rho) , \tag{47}$$

where the functions $X^{\pm}_{L'L}(\boldsymbol{\kappa},E,\rho)$ are to be determined from Eq. (46). But here is the essential point: One cannot establish a coupled-channel equation for the coefficients $X^{\pm}_{L'L}(\boldsymbol{\kappa},E,\rho)$ because the spherical functions $Y_L(\hat{\rho})$ are orthogonal on the surface of the sphere and, therefore, for $\rho>\mu$, the radius of the inscribed sphere, one cannot introduce Eq. (47) into Eq. (46) and use the orthogonality of the spherical functions.[26]

It turns out that this difficulty can be overcome by constructing a prolongation of $\Psi^{\pm}_{L}(\boldsymbol{\kappa},E,\boldsymbol{\rho})$ in a spherical domain which includes the unit cell, and by finding the multipole expansion of this prolongation.[26] Obviously, one can choose various prolongations, but we focus here on the Bloch-periodic prolongation $\Psi^{d\pm}_{L}(\boldsymbol{\kappa},E,\mathbf{r})$ as defined by

$$\begin{gathered}\Psi^{d\pm}_{L}(\boldsymbol{\kappa},E,\boldsymbol{\rho}+\mathbf{R})=e^{i\boldsymbol{\kappa}\mathbf{R}}\Psi^{\pm}_{L}(\boldsymbol{\kappa},E,\boldsymbol{\rho}) ,\\ \nabla\Psi^{d\pm}_{L}(\boldsymbol{\kappa},E,\boldsymbol{\rho}+\mathbf{R})=e^{i\boldsymbol{\kappa}\mathbf{R}}\nabla\Psi^{\pm}_{L}(\boldsymbol{\kappa},E,\boldsymbol{\rho}) ,\end{gathered} \tag{48}$$

for any $\mathbf{r}=\boldsymbol{\rho}+\mathbf{R}$ with $r\le d$ and arbitrary d. Among various possible prolongations, the function $\Psi^{d\pm}_{L}(\boldsymbol{\kappa},E,\mathbf{r})$ has a privileged position. Being given by the right-hand side (rhs) of Eq. (46) by taking $\boldsymbol{\rho}\rightarrow\mathbf{r}$ [from Eqs. (9) and (24)], the coupled-channel equation for its multipole expansion can be easily derived. Thus, by using essentially the same arguments as in Ref. 16, we conclude from Eq. (46) that the prolongation defined by Eq. (48) can be given in the form

$$\Psi^{d\pm}_{L}(\boldsymbol{\kappa},E,\mathbf{r})=\sum_{L'}\Phi^{d}_{L'}(E,\mathbf{r})A^{\pm}_{L'L}(\boldsymbol{\kappa},E),\quad r\le d , \tag{49}$$

where the coefficients $A^{\pm}_{L'L}(\boldsymbol{\kappa},E)$ are functionals of $\Psi^{\pm}_{L}(\boldsymbol{\kappa},E,\boldsymbol{\rho})$,

$$A^{\pm}_{L'L}(\boldsymbol{\kappa},E)=J_{L'L}(\boldsymbol{\kappa},E)+\frac{\mp i\pi\sqrt{E}}{2}\int_{\Omega}h^{\mp *}_{L'}(\boldsymbol{\kappa},E,\boldsymbol{\rho})\mathcal{V}(\boldsymbol{\rho})\times\Psi^{\pm}_{L}(\boldsymbol{\kappa},E,\boldsymbol{\rho})d\boldsymbol{\rho} . \tag{50}$$

[Note that the coefficients $A^{\pm}_{L'L}(\boldsymbol{\kappa},E)$ are independent of d.] Here we introduced the abbreviation [compare with Eq. (24)]

$$\begin{gathered}n_L(\boldsymbol{\kappa},E,\boldsymbol{\rho})=\sum_{\mathbf{R}}e^{-i\boldsymbol{\kappa}\cdot\mathbf{R}}n_L(E,\boldsymbol{\rho}+\mathbf{R}) ,\\ h^{\pm}_{L}(\boldsymbol{\kappa},E,\boldsymbol{\rho})=j_L(\boldsymbol{\kappa},E,\boldsymbol{\rho})\pm in_L(\boldsymbol{\kappa},E,\boldsymbol{\rho}) ,\end{gathered} \tag{51}$$

and the functions $\Phi^{d}_{L}(E,\mathbf{r})$ are defined by

$$\begin{gathered}(\Delta+E)\Phi^{d}_{L}(E,\mathbf{r})=V^{d}\Phi^{d}_{L}(E,\mathbf{r}) ,\\ \Phi^{d}_{L}(E,\mathbf{r})\underset{r\rightarrow 0}{\longrightarrow}j_L(E,\mathbf{r}) ,\end{gathered} \tag{52a}$$

with the potential V^d defined in Eq. (4), and have the obvious property

$$\Phi^{d}_{L}(E,\mathbf{r})=\Phi^{d'}_{L}(E,\mathbf{r})\quad\text{for } r\le\min(d,d') \tag{52b}$$

[compare Eqs. (49), (50), and (52a) with those of the usual scattering theory, Eqs. (A18), (A17), and (A19), respectively].

Obviously, in the limit $d\rightarrow\infty$, Eq. (49) gives the Bloch periodic extension of the function $\Psi^{\pm}_{L}(\boldsymbol{\kappa},E,\boldsymbol{\rho})$ in the whole space. Then, the Bloch function in the unit cell, which is needed in Eq. (50), can be obtained by a folding-back procedure. We introduce the (Bloch periodic) functions (for d larger than the radius of the circumscribing sphere)

$$\begin{aligned}\tilde{\Phi}^{d}_{L}(\boldsymbol{\kappa},E,\boldsymbol{\rho})&=\frac{1}{n^{d}(\boldsymbol{\rho})}\sum_{\mathbf{R},\ |\boldsymbol{\rho}+\mathbf{R}|\le d}e^{-i\boldsymbol{\kappa}\cdot\mathbf{R}}\Phi^{d}_{L}(E,\boldsymbol{\rho}+\mathbf{R})\\ &=\Phi^{\mathrm{circ}}_{L}(E,\boldsymbol{\rho})+\Delta^{d}_{L}(\boldsymbol{\kappa},E,\boldsymbol{\rho}) ,\end{aligned} \tag{53a}$$

$$\begin{aligned}\tilde{\Phi}_{L}(\boldsymbol{\kappa},E,\boldsymbol{\rho})&=\lim_{d\rightarrow\infty}\tilde{\Phi}^{d}_{L}(\boldsymbol{\kappa},E,\boldsymbol{\rho})\\ &=\Phi^{\mathrm{circ}}_{L}(E,\boldsymbol{\rho})+\lim_{d\rightarrow\infty}\Delta^{d}_{L}(\boldsymbol{\kappa},E,\boldsymbol{\rho}) ,\end{aligned} \tag{53b}$$

$$\Delta^{d}_{L}(\boldsymbol{\kappa},E,\boldsymbol{\rho})=\frac{1}{n^{d}(\boldsymbol{\rho})}\sum_{\mathbf{R}\neq 0,\ |\boldsymbol{\rho}+\mathbf{R}|\le d}[e^{-i\boldsymbol{\kappa}\cdot\mathbf{R}}\Phi^{d}_{L}(E,\boldsymbol{\rho}+\mathbf{R})-\Phi^{\mathrm{circ}}_{L}(E,\boldsymbol{\rho})] , \tag{53c}$$

where $n^d(\boldsymbol{\rho})$ represents the number of translations $\mathbf{R}$ which leave the point $\boldsymbol{\rho}$ inside the sphere with radius d, $\Phi_L^{\text{circ}}(E,\boldsymbol{\rho})$ corresponds to d, the radius of the circumscribing sphere, and the property (52b) was taken into account.[16] Then, the function $\Psi_L^{\pm}(\boldsymbol{\kappa},E,\boldsymbol{\rho})$ can be represented as a superposition of Bloch periodic functions

$$\begin{aligned}\Psi_L^{\pm}(\boldsymbol{\kappa},E,\boldsymbol{\rho}) &= \sum_{L'} \tilde{\Phi}_{L'}(\boldsymbol{\kappa},E,\boldsymbol{\rho}) A_{L'L}^{\pm}(\boldsymbol{\kappa},E) \\ &= \lim_{d\to\infty} \sum_{L'} \tilde{\Phi}_{L'}^{d}(\boldsymbol{\kappa},E,\boldsymbol{\rho}) A_{L'L}^{\pm}(\boldsymbol{\kappa},E) \;, \end{aligned} \tag{54a}$$

or as a superposition in the linear space of regular solutions of Eq. (52a)

$$\Psi_L^{\pm}(\boldsymbol{\kappa},E,\boldsymbol{\rho}) = \sum_{L'} \Phi_{L'}^{\text{circ}}(E,\boldsymbol{\rho}) A_{L'L}^{\pm}(\boldsymbol{\kappa},E) \;. \tag{54b}$$

Here the coefficients $A_{L'L}^{\pm}(\boldsymbol{\kappa},E)$ are given by [from Eqs. (50) and (54)]

$$\sum_{L''} \left[\delta_{L'L''} + \frac{\pm i\pi\sqrt{E}}{2} \int_{\Omega} h_{L'}^{\mp *}(\boldsymbol{\kappa},E,\boldsymbol{\rho}) \mathcal{V}(\boldsymbol{\rho}) \tilde{\Phi}_{L''}(\boldsymbol{\kappa},E,\boldsymbol{\rho}) \right] A_{L''L}^{\pm}(\boldsymbol{\kappa},E) = J_{L'L}(\boldsymbol{\kappa},E) \;, \tag{55a}$$

which, providing $E \neq E_n(\boldsymbol{\kappa})$, can be solved[16] by taking the inverse of the matrix in the lhs of Eq. (55a). Thus, Eq. (38) now becomes [compare with Eq. (A21)]

$$\begin{aligned}\mathcal{T}_{L'L}^{\pm}(\boldsymbol{\kappa},E) = \sum_{L''} \Bigg[&\int_{\Omega} \Psi_{0_{L'}}^{*}(\boldsymbol{\kappa},E,\boldsymbol{\rho}) \mathcal{V}(\boldsymbol{\rho}) \\ &\times \tilde{\Phi}_{L''}(\boldsymbol{\kappa},E,\boldsymbol{\rho}) d\boldsymbol{\rho} \Bigg] A_{L''L}^{\pm}(\boldsymbol{\kappa},E) \;, \end{aligned} \tag{55b}$$

where we recall the definition Eq. (24) and properties (35). [Notice the fact that, in general, Eq. (49) or (54b) cannot be introduced into Eq. (50) and integrated term by term to give a linear system for the coefficients $A_{L'L}^{\pm}(\boldsymbol{\kappa},E)$.[27] Instead, for $d \to \infty$ we can use Eqs. (53a) and (53b) in Eq. (55) to obtain successive approximations for the coefficients $A_{L'L}^{\pm}(\boldsymbol{\kappa},E)$ which, in the limit, represents the exact result. Obviously, a natural approximation would be to retain only the first term in Eq. (53b) and thus obtaining[16] the "generalized muffin-tin approximation." In particular, this includes the case of a muffin-tin potential. A more detailed discussion of the effect of various approximations is given in Sec. IV, below.]

Following the line of Ref. 16 (and in view of the comparison with the muffin-tin case described in the Appendix), it is advantageous to introduce the matrices $\underline{\Sigma}^d(\boldsymbol{\kappa},E)$ and $\underline{\Gamma}^d(\boldsymbol{\kappa},E)$ having the matrix elements [compare with Eq. (A22)]

$$\begin{aligned}\Gamma_{L'L}^{d}(\boldsymbol{\kappa},E) &= \delta_{L'L} - \frac{\pi\sqrt{E}}{2} \int_{\Omega} n_{L'}^{*}(E,\boldsymbol{\rho}) \mathcal{V}(\boldsymbol{\rho}) \tilde{\Phi}_{L}^{d}(\boldsymbol{\kappa},E,\boldsymbol{\rho}) d\boldsymbol{\rho} \;, \\ \Sigma_{L'L}^{d}(\boldsymbol{\kappa},E) &= \frac{\pi\sqrt{E}}{2} \int_{\Omega} j_{L'}^{*}(E,\boldsymbol{\rho}) \mathcal{V}(\boldsymbol{\rho}) \tilde{\Phi}_{L}^{d}(\boldsymbol{\kappa},E,\boldsymbol{\rho}) d\boldsymbol{\rho} \;, \end{aligned} \tag{56a}$$

as well as the matrix [cf. Eq. (A23)]

$$\underline{\Theta}^{d\pm}(\boldsymbol{\kappa},E) = \underline{\Sigma}^{d}(\boldsymbol{\kappa},E)[\underline{\Gamma}^{d}(\boldsymbol{\kappa},E) \pm i\underline{\Sigma}^{d}(\boldsymbol{\kappa},E)]^{-1} \;. \tag{56b}$$

The limit $d \to \infty$ in Eqs. (56) is denoted by removing the index d. In contradistinction to the muffin-tin case, Eqs. (A22) and (A23), the matrices $\underline{\Sigma}^d(\boldsymbol{\kappa},E)$ and $\underline{\Gamma}^d(\boldsymbol{\kappa},E)$ contain information on both the structure [from Eq. (53a)] and the potential [from Eq. (52)] inside the sphere with radius $d \to \infty$. In other words, these matrices contain a supplementary $\boldsymbol{\kappa}$ dependence which comes from the correct use in Eq. (50) of the Bloch periodic superposition Eq. (54a) and not of Eq. (54b).[27] However, they can be expressed in the form [from Eqs. (53a) and (53b)]

$$\begin{aligned}\Sigma_{L'L}^{d}(\boldsymbol{\kappa},E) &= \Sigma_{L'L}^{\text{circ}}(E) + \frac{\pi\sqrt{E}}{2} \int_{\Omega} j_{L'}^{*}(E,\boldsymbol{\rho}) \mathcal{V}(\boldsymbol{\rho}) \\ &\qquad \times \Delta_{L}^{d}(\boldsymbol{\kappa},E,\boldsymbol{\rho}) d\boldsymbol{\rho} \;, \\ \Gamma_{L'L}^{d}(\boldsymbol{\kappa},E) &= \Gamma_{L'L}^{\text{circ}}(E) - \frac{\pi\sqrt{E}}{2} \int_{\Omega} n_{L'}^{*}(E,\boldsymbol{\rho}) \mathcal{V}(\boldsymbol{\rho}) \\ &\qquad \times \Delta_{L}^{d}(\boldsymbol{\kappa},E,\boldsymbol{\rho}) d\boldsymbol{\rho} \;, \end{aligned} \tag{57}$$

where the matrices

$$\begin{aligned}\Sigma_{L'L}^{\text{circ}}(E) &= \frac{\pi\sqrt{E}}{2} \int_{\Omega} j_{L'}^{*}(E,\boldsymbol{\rho}) \mathcal{V}(\boldsymbol{\rho}) \Phi_{L}^{\text{circ}}(E,\boldsymbol{\rho}) d\boldsymbol{\rho} \;, \\ \Gamma_{L'L}^{\text{circ}}(E) &= \delta_{L'L} - \frac{\pi\sqrt{E}}{2} \int_{\Omega} n_{L'}^{*}(E,\boldsymbol{\rho}) \mathcal{V}(\boldsymbol{\rho}) \Phi_{L}^{\text{circ}}(E,\boldsymbol{\rho}) d\boldsymbol{\rho} \;, \end{aligned} \tag{58}$$

and similarly for $\underline{\Theta}^{\text{circ}}(\boldsymbol{\kappa},E)$, now express only the potential (but within the inscribed sphere) akin to the muffin-tin case, Eqs. (A22) and (A23). The second term in Eq. (57) (which still contains both the structure and the potential) is expected to represent a correction.[16] [We notice in advance, that this term reflects the correct consideration of the periodicity and, therefore, it is not related with the usual "near-field" corrections,"[12] which are mostly connected with the convergence of the multipole expansion of the Green function defined in Eq. (A5).][28] Finally, from the translational properties of the Bessel and Neumann functions[23] we always have

$$\begin{aligned}\frac{\pi\sqrt{E}}{2} &\int_{\Omega} j_{L'}^{*}(\boldsymbol{\kappa},E,\boldsymbol{\rho}) \mathcal{V}(\boldsymbol{\rho}) \tilde{\Phi}_{L}^{d}(\kappa,E,\boldsymbol{\rho}) d\boldsymbol{\rho} \\ &= \sum_{L''} J_{L'L''}(\boldsymbol{\kappa},E) \Sigma_{L''L}^{d}(\boldsymbol{\kappa},E) \;. \end{aligned} \tag{59}$$

By contrast, the matrix

$$\mathfrak{G}^d_{L'L}(\boldsymbol{\kappa},E)=\frac{\pi\sqrt{E}}{2}\int_{\Omega}\left[\sum_{\mathbf{R}\neq 0}e^{-i\boldsymbol{\kappa}\cdot\mathbf{R}}n^{*}_{L'}(E,\boldsymbol{\rho}+\mathbf{R})\right]\times\mathcal{V}(\boldsymbol{\rho})\tilde{\Phi}^{d}_{L}(\boldsymbol{\kappa},E,\boldsymbol{\rho})d\boldsymbol{\rho} \tag{60}$$

can be written (factorized) in terms of the structure constants

$$\underline{\mathfrak{G}}^d(\boldsymbol{\kappa},E)=\underline{\mathrm{N}}(\boldsymbol{\kappa},E)\underline{\Sigma}^d(\boldsymbol{\kappa},E) \tag{61}$$

only in the case of close-packed lattices, i.e., $\max_{\rho\in\Omega}\rho<\min R$, which includes the muffin-tin case. In Eq. (61) we introduced the structure constant[2,3] $N_{L'L}(\boldsymbol{\kappa},E)$ as defined by

$$\begin{aligned}N_{L'L}(\boldsymbol{\kappa},E)&=\sum_{\mathbf{R}\neq 0}e^{-i\boldsymbol{\kappa}\cdot\mathbf{R}}N_{L'L}(E,\mathbf{R})\ ,\\ N_{L'L}(E,\mathbf{R})&=\sum_{L''}I^{L}_{L'L''}N_{L''L}(E,\mathbf{R})\end{aligned} \tag{62}$$

[compare with Eqs. (30) and (32)], and which satisfy similar properties to that expressed by Eqs. (31c) and (34c). Clearly, the troubles with the existence of the factorization, Eq. (61), come from the contribution of the nearest neighbors; in this view, the existence of Eq. (61) is connected with the usual near-field correction (as discussed in Ref. 12 and references therein).

Now we come back to the matrix element, Eqs. (55b), (23), and (22a) which, by using the notation Eqs. (56)–(62), can be written as [compare with Eq. (A12)]

$$\underline{\mathrm{T}}^{\pm}(E)=\frac{2}{\pi\sqrt{E}}\int_{\tilde{\Omega}}\frac{d\boldsymbol{\kappa}}{\tilde{\omega}}\underline{J}(\boldsymbol{\kappa},E)\underline{\mathfrak{T}}^{\pm}(\boldsymbol{\kappa},E)\underline{J}(\boldsymbol{\kappa},E)\ , \tag{63}$$

where $\mathfrak{T}^{\pm}(\boldsymbol{\kappa},E)$ denotes the matrix

$$\underline{\mathfrak{T}}^{\pm}(\boldsymbol{\kappa},E)=\{\underline{\Theta}^{\pm}(\boldsymbol{\kappa},E)^{-1}\pm i[\underline{J}(\boldsymbol{\kappa},E)-1\pm i\underline{\mathfrak{G}}(\boldsymbol{\kappa},E)\underline{\Sigma}(\boldsymbol{\kappa},E)^{-1}]\}^{-1}\ . \tag{64}$$

In the case of close-packed lattices, i.e., $\max_{\rho\in\Omega}\rho<\min R$, by using Eq. (61), Eq. (64) further becomes [compare with Eq. (A13)]

$$\underline{\mathfrak{T}}^{\pm}(\boldsymbol{\kappa},E)=[\underline{\Theta}^{\pm}(\boldsymbol{\kappa},E)^{-1}\pm i\underline{H}^{\pm}(\boldsymbol{\kappa},E)]^{-1}\ , \tag{65}$$

where we introduced the structure constant

$$\begin{aligned}H^{\pm}_{LL'}(\boldsymbol{\kappa},E)&=\sum_{\mathbf{R}\neq 0}e^{-i\boldsymbol{\kappa}\cdot\mathbf{R}}H^{\pm}_{LL'}(E,\mathbf{R})\\ &=J_{LL'}(\boldsymbol{\kappa},E)-\delta_{LL'}\pm iN_{LL'}(\boldsymbol{\kappa},E)\ ,\\ H^{\pm}_{LL'}(E,\mathbf{R})&=\sum_{L''}I^{L'}_{LL''}h^{\pm}_{L''}(E,\mathbf{R})\quad\text{for }\mathbf{R}\neq 0\\ H^{\pm}_{LL'}(E,\mathbf{R})&=0\quad\text{for }\mathbf{R}=0\ .\end{aligned} \tag{66}$$

Since the quantities which appear in Eq. (63) depend on $\boldsymbol{\kappa}$ only by means of a sum, $\sum_R e^{-i\boldsymbol{\kappa}\cdot\mathbf{R}}f(\mathbf{R})$, it is possible to express the integration over the Brillouin zone as a summation over the lattice vectors $\mathbf{R}$. Actually, by using Eqs. (8), (31), and (34a), we obtain in the case of close-packed lattices [compare with Eq. (A9)]

$$\underline{\mathrm{T}}^{\pm}(E)=\frac{2}{\pi\sqrt{E}}\sum_{\mathbf{R},\mathbf{R}'}\underline{J}(E,-R)\underline{\mathfrak{T}}^{\pm}(E,\mathbf{R}-\mathbf{R}')\underline{J}(E,\mathbf{R}')\ , \tag{67}$$

where $\mathfrak{T}^{\pm}(E,\mathbf{R}-\mathbf{R}')$ denotes the matrix (lattice Fourier transform) [cf. Eq. (A10)]

$$\mathfrak{T}^{\pm}(E,\mathbf{R}-\mathbf{R}')=\underline{\Theta}^{\pm}(\boldsymbol{\kappa},E)[\delta_{\mathbf{RR}'}\pm i\underline{H}^{\pm}(E,\mathbf{R}-\mathbf{R}')\underline{\Theta}^{\pm}(\boldsymbol{\kappa},E)]^{-1}\ , \tag{68}$$

and the inverse is taken in the site representation. (So far, we have encountered only inverses in the L representation.) In fact, Eq. (68) represents a generalization of the (muffin-tin) scattering path operator.[13] Finally, one can see that the poles of the $T^{\pm}(E)$ matrix represent the energy levels as given by the band-structure equation derived in Ref. 16 (and proven in the soluble case of constant periodic potential to yield the correct solution).

IV. EFFECTS OF VARIOUS APPROXIMATIONS AND THEIR RELATION TO PREVIOUS APPROXIMATE RESULTS

Equations (63)–(65), (67), and (68) represent our main results. They give the on-shell matrix elements of the $T^{\pm}(E)$ operators in the L representation for a general (non-muffin-tin) periodic potential. These equations have the advantage of describing the periodic potential in spherical coordinates and thus avoiding the plane-wave expansions (which are slowly convergent). [Recall that it is the folding procedure, Eqs. (24), (25), and (53), which ultimately allows for this description in spherical coordinates.]

The poles of the matrix elements, Eqs. (64) or (65), generate the same band-structure equation as that derived in Ref. 16 and proven (in contradistinction to the previous attempts,[9,10] claimed as exact) to generate correct results in a soluble case. Further, being an exact result, Eqs. (63)–(65), (67), and (68) contribute to a better understanding of the periodic potential problem in relation to the usual case of a potential which falls down at infinity. In particular, they illustrate the extent to which the notion of the phase-shift operator of the usual scattering theory survives in the case of a periodic operator which does not allow for asymptotic free regions. Also, their close similarity to the corresponding equations of the muffin-tin case suggests further investigations for the existence of a Friedel-type sum rule[29] or for possible expressions of the charge density in terms of the matrices $\underline{\Sigma}(\boldsymbol{\kappa},E)$ and $\underline{\Gamma}(\boldsymbol{\kappa},E)$ akin to the muffin-tin case.[3] Finally, being an exact result, Eqs. (63)–(65), (67), and (68) may serve as a base for further approximations which we now discuss.

Let us first examine the essential difference between the general periodic potential and the muffin-tin case.[3] Compare then Eqs. (63)–(65), (67), and (68) for the general periodic potential with Eqs. (A12), (A13), (A9) and (A10) for the muffin-tin case, respectively. In the case of close-packed lattices, the only distinction is made by a supplementary $\boldsymbol{\kappa}$ dependence of the matrix $\underline{\Theta}^{\pm}(\boldsymbol{\kappa},E)$, Eq. (56b), i.e., by the presence of "Bloch periodicity corrections" discussed in detail in Ref. 16. In other words, the geometry of the lattice is not only contained in the structure constants but also in the matrix $\underline{\mathfrak{G}}$ which no longer represents the t matrix of the unit cell, Eq. (A11). [In fact, this supplementary $\boldsymbol{\kappa}$ dependence of the cell potential contribution represents, ultimately, our main result; previous attempts tried to produce results (claimed exact) by using, in one way or the other, the decomposition Eqs. (A5) and (A6) in Eqs. (A1)–(A3),[28] whereas the present formalism relies on Eqs. (10), (13), (50), and (54b).] In the general case there is an additional difference caused by the matrix $\mathfrak{C}$ which cannot be factorized, Eq. (61), unless the condition $\max_{\rho\in\Omega}\rho\leq\min R$ is satisfied. (By the way, this clearly shows the relation between structure and potential in the case of a general periodic potential.)

By confining ourselves to the close-packed lattices, the problem is how to approximate in a simpler form the $\boldsymbol{\kappa}$ dependence of the matrix $\underline{\Theta}^{\pm}(\boldsymbol{\kappa},E)$ in Eq. (65). [As was mentioned before, this $\boldsymbol{\kappa}$ dependence comes from a correct consideration of the periodicity, that is, in Eq. (50) one should use Eq. (54a) and not Eq. (54b).] An easy way will be to drop this dependence, that is to neglect the second term in Eq. (53a) and hence in Eq. (57); in this case, the structure becomes separated from the potential but, unless the potential is of muffin-tin type, the corresponding matrix $\underline{\Theta}^{\text{circ}}(\boldsymbol{\kappa},E)$ is not yet the t matrix of the unit cell. While it yields a band-structure equation (derived in Ref. 9 by other means and believed by these authors to be an exact result) this approximation violates the Bloch periodicity of the function $\Phi_L(\boldsymbol{\kappa},E,\boldsymbol{\rho})$ in Eq. (55a) on the boundary of the unit cell; in this respect, it is equivalent[16] to the approximation made by replacing the functions Φ^{circ} (determined by the potential in the circumscribed sphere) with the regular solutions, Eq. (52a), of the cell potential $\mathcal{V}$. In this approximation the structure is not only separated from the potential, but the corresponding matrix Θ^{cell} becomes the t matrix of the unit cell, as in the muffin-tin case (see also the final remarks in the Appendix). This approximate result was derived previously, by other means, in Refs. 11 and 15; in Ref. 10 it is given as an exact result. From the computational point of view of the band-structure calculations, these two approximations are equivalent and in the particular case of a constant potential and a cubic lattice, they yield satisfactory accuracy.[9,12] However, these approximations also give a systematic displacement (from the correct values) which cannot be diminished by increasing the dimension of the L space.[12] In fact, these two approximations express the same physics, namely, the "generalized muffin-tin approximation," when the cell potential is zero near the boundary of the unit cell. Actually, in this case we need the function $\Psi_L^{\pm}(\boldsymbol{\kappa},E,\boldsymbol{\rho})$ in Eq. (50) only for an *interior* domain of the unit cell, where this function can be equally represented by Eq. (54a) or Eq. (54b) or as a superposition of the regular solutions of the cell potential.[16,27]

A better approximation is to consider a reasonably large d in Eq. (53a). In particular, the choice of the radius of the circumscribing sphere [when the function $n^d(\boldsymbol{\rho})$ takes only the values 2 or 3 for a square lattice] requires essentially the same computational effort as do previous approximations,[9] but represents a first attempt to correctly consider the periodicity, when described in spherical coordinates by means of multipole expansions.

V. SUMMARY AND CONCLUSIONS

We considered a general periodic potential and derived (from the periodicity alone) that the $T^{\pm}(E)$ operators, as defined in Eq. (5), can be written as an integral over the Brillouin zone, Eq. (10), from the reduced $\mathcal{T}^{\pm}(\boldsymbol{\kappa},E)$ operators defined in Eq. (13). Thus, the study of the total operators $T^{\pm}(E)$ was simplified to the study of the reduced operators $\mathcal{T}^{\pm}(\boldsymbol{\kappa},E)$. In particular, the matrix elements $T^{\pm}_{\lambda\lambda'}(E)$, cf. Eqs. (20) and (21), where λ stands for L or $\hat{\mathbf{p}}$, are given, Eqs. (22), in terms of the reduced matrix elements $\mathcal{T}^{\pm}_{\lambda\lambda'}(\boldsymbol{\kappa},E)$. These matrix elements are calculated in a formalism which is very close to that of the usual scattering theory: By introducing the Bloch periodic in and out states, Eq. (37), the reduced operators $\mathcal{T}^{\pm}(\boldsymbol{\kappa},E)$ (on-shell part) are shown to transform Bloch periodic "scattering states" into Bloch periodic "free states," Eq. (38). Both these Bloch periodic free and scattering states have a distributional character but this is not too troublesome because we are interested in calculating only integrals, and not point-by-point values. Finally, the on-shell matrix elements were worked out in both the plane-wave representation, Eqs. (43)–(45), and in the L representation, Eqs. (63)–(67).

In the L representation, the functional form of the matrix elements, cf. Eqs. (63)–(67), is very close to that of the muffin-tin case, Eqs. (A9)–(A13), but the contribution of the structure is no longer separated from that of the potential. In the case of close-packed lattices, Eqs. (61) and (65), the structure constants appear in the same way as in the case of the muffin-tin potential, Eq. (A10), but the matrices $\underline{\Sigma}^d(\boldsymbol{\kappa},E)$, $\underline{\Gamma}^d(\boldsymbol{\kappa},E)$, and $\underline{\Theta}^d(\boldsymbol{\kappa},E)$ depend on both $\boldsymbol{\kappa}$ and E (i.e., on both the structure and the potential). This supplementary $\boldsymbol{\kappa}$ dependence comes from a correct consideration of the periodicity;[16] it is therefore different from the usual near-field corrections which are instead connected in this formalism with the factorization of the matrix $\underline{\mathfrak{G}}(\boldsymbol{\kappa},E)$, Eqs. (60) and (61), and then with convergence of the L series.[12] Further, this supplementary dependence can be given a considerable simplification by introducing various approximations into Eq. (53) [and hence in Eqs. (57) and (58)] and then, rediscovering previously known (approximate) results[9,11,14] (and claimed by several authors[9,10] to be exact). Finally, the poles of the on-shell T matrix give the same band structure as a previously determined band structure-equation[16] which, in turn, was proven (analytically) to be equivalent to the usual plane-wave diagonalization (taken as an exact result).

ACKNOWLEDGMENT

This work was supported by the National Science Foundation (DMR Grant No. 85-18607).

APPENDIX: ON-SHELL $T^{\pm}$ MATRIX FOR THE MUFFIN-TIN POTENTIAL

As a way of enhancing the generality (and hence the power) of the present approach, we briefly recall here the usual multiple-scattering derivation of the on-shell $T^{\pm}$ matrix for the case of a muffin-tin periodic potential.[3,13,14] (This also serves to indicate its novelty and its ability to overcome the difficulties of the multiple-scattering approach.) We present this derivation using the same notation given in the main text so as to facilitate (i) easy comparisons between the two cases and (ii) an understanding of their differences as well as of the limitations of the multiple-scattering approach.

Consider then a periodic potential as defined in Eq. (2) and notice that Eq. (5) can be put in the form[3]

$$T^{\pm}(E)=\sum_{\mathbf{R}} t_{\mathbf{R}}^{\pm}(E)+\sum_{\mathbf{R}\neq\mathbf{R}'} t_{\mathbf{R}}^{\pm}(E)G_0^{\pm}(E)t_{\mathbf{R}'}^{\pm}(E)+\cdots\ , \tag{A1}$$

where the $[L^2(R^3)]$ kernel of the Green function $G^{\pm}(E)$ is given in Eq. (6) and $t_{\mathbf{R}}^{\pm}(E)$ denotes the $T^{\pm}$ operator corresponding to the potential $\mathcal{V}_{\mathbf{R}}$ (as if all the other cells were absent); hence, the $[L^2(R^3)]$ kernel $t_R^{\pm}(E,\mathbf{r},\mathbf{r}')$ of the operator $t_{\mathbf{R}}^{\pm}(E)$ has the property

$$t_{\mathbf{R}}^{\pm}(E,\mathbf{r},\mathbf{r}')=\begin{cases} t^{\pm}(E,\boldsymbol{\rho},\boldsymbol{\rho}') & \text{if } \mathbf{r}=\mathbf{R}+\boldsymbol{\rho} \text{ and } \mathbf{r}'=\mathbf{R}+\boldsymbol{\rho}' \\ 0 & \text{otherwise,}\end{cases} \tag{A2}$$

and the function $t^{\pm}(E,\boldsymbol{\rho},\boldsymbol{\rho}')$ defines the $[L^2(R^3)]$ operator

$$t^{\pm}(E)=\mathcal{V}+\mathcal{V}G_0^{\pm}(E)t^{\pm}(E)\ , \tag{A3}$$

where $\mathcal{V}$ is the potential defined in Eq. (3b). Apparently, the operator $t^{\pm}(E)$ has the property

$$\begin{aligned} &t^{\pm}(E,\mathbf{r},\mathbf{r}')=0 \quad \text{for those } \mathbf{r} \text{ or } \mathbf{r}' \text{ for which} \\ &\qquad\qquad \mathcal{V}(\mathbf{r}) \text{ or } \mathcal{V}(\mathbf{r}') \text{ is zero} \\ &t^{\pm}(E,\mathbf{r},\mathbf{r}')\neq 0 \quad \text{otherwise}\ . \end{aligned} \tag{A4}$$

Now, Eqs. (A1)–(A3) hold irrespective of whether the periodic potential is of muffin-tin type or not.[30] However, in the muffin-tin case, i.e., $\mathcal{V}(\mathbf{r})=0$ for $r>\mu$ in Eq. (A3), Eqs. (A1)–(A3) can be further exploited to result in a closed expression for the on-shell matrix elements. Actually, in this case, Eq. (A1) involves the Green function [from Eq. (A4)]

$$G_0^{\pm}(E,\mathbf{R}+\boldsymbol{\rho},\mathbf{R}'+\boldsymbol{\rho}')=\frac{1}{4\pi}\frac{e^{\pm i\sqrt{E}\,|\boldsymbol{\rho}+\mathbf{R}-\mathbf{R}'-\boldsymbol{\rho}'|}}{|\boldsymbol{\rho}+\mathbf{R}-\mathbf{R}'-\boldsymbol{\rho}'|}\ , \quad \mathbf{R}\neq\mathbf{R}'\ , \tag{A5}$$

only for the interior points of the muffin-tin spheres, i.e., $\rho,\rho'\leq\mu$, for which situation we have the (on-shell) decomposition[28]

$$\begin{aligned} &G_0^{\pm}(E,\mathbf{R}+\boldsymbol{\rho},\mathbf{R}'+\boldsymbol{\rho}') \\ &\quad=\frac{\mp i\pi\sqrt{E}}{2}\sum_{L,L'} j_L(E,\boldsymbol{\rho})H_{LL'}^{\pm}(E,\mathbf{R}-\mathbf{R}')j_{L'}^{*}(E,\boldsymbol{\rho}')\ , \end{aligned} \tag{A6}$$

where the matrix (structure constant) $H_{LL'}^{\pm}(E,\mathbf{R})$ is given in Eq. (66). Then, by using Eq. (A6) in Eq. (A1), we find that only the on-shell matrix elements

$$t_{L'L}^{\mathrm{mt}\pm}(E)=\int j_{L'}^{*}(E,\mathbf{r})t^{\mathrm{mt}\pm}(E,\mathbf{r},\mathbf{r}')j_L(E,\mathbf{r})d\mathbf{r} \tag{A7}$$

are involved, where the superscript mt emphasizes the muffin-tin case. Further, by using Eqs. (29) and (31c), as in Ref. 3, we find the matrix elements

$$T_{L'L}^{\mathrm{mt}\pm}(E)=\int j_{L'}^{*}(E,\mathbf{r})T^{\mathrm{mt}\pm}(E,\mathbf{r},\mathbf{r}')j_L(E,\mathbf{r})d\mathbf{r} \tag{A8}$$

in the form (hereafter, the bold letters denote matrices in the L representation),

$$\underline{\mathbf{T}}^{\mathrm{mt}\pm}(E)=\frac{2}{\pi\sqrt{E}}\sum_{\mathbf{R},\mathbf{R}'}\underline{J}(E,-R)\underline{\mathfrak{T}}^{\mathrm{mt}\pm}(E,\mathbf{R}-\mathbf{R}')\underline{J}(E,\mathbf{R}')\ , \tag{A9}$$

where the matrix $J(E,\mathbf{R})$ was defined in Eq. (30) and we introduced the matrix

$$\begin{aligned} &\underline{\mathfrak{T}}^{\mathrm{mt}\pm}(E,\mathbf{R}-\mathbf{R}') \\ &\quad=\underline{\Theta}^{\pm}(E)\delta_{\mathbf{R}\mathbf{R}'}\mp i\sum_{\mathbf{R},\mathbf{R}'}\underline{\Theta}^{\pm}(E)\underline{H}^{\pm}(E,\mathbf{R}-\mathbf{R}')\underline{\Theta}^{\pm}(E)+\cdots \\ &\quad=\underline{\Theta}^{\pm}(E)[\delta_{\mathbf{R}\mathbf{R}'}\pm i\underline{H}^{\pm}(E,\mathbf{R},\mathbf{R}')\underline{\Theta}^{\pm}(E)]^{-1}\ . \end{aligned} \tag{A10}$$

Here the inverse is taken in the site representation and $\underline{\Theta}^{\pm}(E)$ denotes the matrix [see Eq. (A7)]

$$\underline{\Theta}^{\pm}(E)=\frac{\pi\sqrt{E}}{2}\underline{t}^{\mathrm{mt}\pm}(E)\ . \tag{A11}$$

[Recall also that the matrix $\underline{H}^{\pm}(E,\mathbf{R})$ is zero for $\mathbf{R}=0$, cf. Eq. (66).]

Alternatively, by using Eqs. (32), (34a), (66), and (8), the sum in Eq. (A9) can be written as an integral over the Brillouin zone

$$\underline{\mathbf{T}}^{\mathrm{mt}\pm}(E)=\frac{2}{\pi\sqrt{E}}\int_{\tilde{\Omega}}\frac{d\boldsymbol{\kappa}}{\tilde{\omega}}\underline{J}(\boldsymbol{\kappa},E)\underline{\mathfrak{T}}^{\mathrm{mt}\pm}(\boldsymbol{\kappa},E)\underline{J}(\boldsymbol{\kappa},E)\ , \tag{A12}$$

where we introduced the matrix

$$\underline{\mathfrak{T}}^{\mathrm{mt}\pm}(\boldsymbol{\kappa},E)=[\underline{\Theta}^{\pm}(E)^{-1}\pm i\underline{H}^{\pm}(\boldsymbol{\kappa},E]^{-1}\ , \tag{A13}$$

and now the inverse is taken in the L representation. It remains then to find the matrix elements $t_{L'L}^{\mathrm{mt}\pm}(E)$, Eqs. (A7) and (A11). Clearly, the calculation of these matrix elements pertains to the ordinary scattering theory[17] [from Eq. (A3)] and has nothing to do with the muffin-tin or non-muffin-tin imposition. Therefore, in what follows we keep the superscript mt only for the potential and for the matrix $t_{L'L}^{\mathrm{mt}\pm}(E)$ but remove this index from the scattering states and regular solutions (because their calculation does not depend on the muffin-tin imposition). Thus, from Eq. (A3), we have[17]

$$t_{L'L}^{\mathrm{mt}\pm}(E)=\int j_{L'}^{*}(E,\mathbf{r})\mathcal{V}^{\mathrm{mt}}(\mathbf{r})\Psi_L^{\pm}(E,\mathbf{r})d\mathbf{r}\ , \tag{A14}$$

where the scattering states $\Psi_L^{\pm}(E,\mathbf{r})$ are given by

$$\Psi_L^{\pm}(E,\mathbf{r})=j_L(E,\mathbf{r})+\int G_0^{\pm}(E,\mathbf{r}')\mathcal{V}^{\mathrm{mt}}(\mathbf{r}')\Psi_L^{\pm}(E,\mathbf{r}')d\mathbf{r}'\ . \tag{A15}$$

Then, we need to solve Eq. (A15); by using Eq. (6) and the behavior of the Bessel and Neuman functions at the origin, we find

$$\Psi_L^{\pm}(E,\mathbf{r}) \underset{\mathbf{r}\to 0}{\longrightarrow} \sum_{L'} j_{L'}(E,\mathbf{r})\alpha_{L'L}^{\pm}(E) \ , \tag{A16}$$

where the coefficients are functionals of $\Psi_L^{\pm}(E,\mathbf{r})$

$$\alpha_{L'L}^{\pm}(E)=\delta_{L'L}+\frac{\mp i\pi\sqrt{E}}{2}\int h_{L'}^{\mp *}(E,\mathbf{r})\mathcal{V}^{\mathrm{mt}}(\mathbf{r})\Psi_L^{\pm}(E,\mathbf{r})d\mathbf{r} \tag{A17}$$

and the potential $\mathcal{V}(\mathbf{r})$ is allowed to have a singularity at the origin behaving, at most as $r^{-2+\epsilon}$, $\epsilon \geq 0$. Since the function $\Psi_L^{\pm}(E,\mathbf{r})$, as solution of Eq. (A15), is uniquely defined, we easily find [from Eqs. (A15) and (A16)]

$$\Psi_L^{\pm}(E,\mathbf{r})=\sum_{L'}\Phi_{L'}(E,\mathbf{r})\alpha_{L'L}^{\pm}(E) \ , \tag{A18}$$

where the functions $\Phi_L(E,\mathbf{r})$ represent the solutions of

$$\begin{gathered}(\Delta+E)\Phi_L(E,\mathbf{r})=\mathcal{V}^{\mathrm{mt}}\Phi_L(E,\mathbf{r}) \ , \\ \Phi_L(E,\mathbf{r}) \underset{r\to 0}{\longrightarrow} j_L(E,\mathbf{r}) \ ,\end{gathered} \tag{A19}$$

and are (relatively easily) computable with the variable phase method.[7,8] We therefore carry on the analysis in terms of these functions. By introducing Eq. (A18) into Eq. (A17), we obtain a linear system for the coefficients

$$\sum_{L''}\left\{\delta_{L'L''}-\frac{\mp i\pi\sqrt{E}}{2}\int h_{L'}^{\mp *}(E,\mathbf{r})\mathcal{V}(\mathbf{r}) \times\Phi_{L''}(E,\mathbf{r})d\mathbf{r}\right\}\alpha_{L''L}^{\pm}(E)=\delta_{L'L} \tag{A20}$$

which has a unique solution if the energy E is not a bound state for a single muffin-tin potential. Then, Eq. (14) becomes

$$t_{L'L}^{\mathrm{mt}\pm}(E)=\sum_{L''}\left\{\int j_{L'}^{*}(E,\mathbf{r})\mathcal{V}^{\mathrm{mt}}(\mathbf{r}) \times\Phi_{L''}(E,\mathbf{r})d\mathbf{r}\right\}\alpha_{L''L}^{\pm}(E) \ . \tag{A21}$$

It is then advantageous to introduce the matrices $\underline{\gamma}(E)$ and $\underline{\sigma}(E)$ as given by[7]

$$\begin{gathered}\gamma_{L'L}(E)=\delta_{L'L}-\frac{\pi\sqrt{E}}{2}\int_{\Omega}n_{L'}^{*}(E,\boldsymbol{\rho})\mathcal{V}^{\mathrm{mt}}(\boldsymbol{\rho})\Phi_L(E,\boldsymbol{\rho})d\boldsymbol{\rho} \ , \\ \sigma_{L'L}(E)=\frac{\pi\sqrt{E}}{2}\int_{\Omega}j_{L'}^{*}(E,\boldsymbol{\rho})\mathcal{V}^{\mathrm{mt}}(\boldsymbol{\rho})\Phi_L(E,\boldsymbol{\rho})d\boldsymbol{\rho} \ ,\end{gathered} \tag{A22}$$

and to write Eqs. (A11), and hence Eqs. (A14) and (A21), in a compact form

$$\underline{\theta}^{\pm}(E)=\underline{\sigma}(E)[\underline{\gamma}(E)\pm i\underline{\sigma}(E)]^{-1} \ . \tag{A23}$$

[It is worthwhile mentioning that the matrices $\underline{\theta}(E)$, $\underline{\sigma}(E)$, and $\underline{\gamma}(E)$ can be found by solving Volterra-type integral equations;[7,8] the equations for $\underline{\sigma}(E)$ and $\underline{\gamma}(E)$ are linear and the equation for $\underline{\theta}(E)$ is quadratic.]

In conclusion, in the expression for the on-shell matrix elements of the total $T^{\mathrm{mt}\pm}$ operators within the multiple-scattering approach[3,13,14], Eqs. (A9) and (A12), the structure (geometry) of the lattice is described only by means of the structure constants $H_{L'L}^{\pm}(\boldsymbol{\kappa},E)$ and $J_{L'L}^{\pm}(\boldsymbol{\kappa},E)$. In this case, then, the structural aspects are decoupled from the potential which enters only by means of the on-shell $t^{\mathrm{mt}\pm}$ matrix of a single muffin-tin potential, Eqs. (A10), (A11), and (A13). In its turn, this matrix is described in terms of the matrices $\underline{\sigma}(E)$ and $\underline{\gamma}(E)$, Eqs. (A21)–(A23) and (A11), which here stand for the "*s*" and "*c*" coefficients of the variable phase method.[7] (These coefficients represent the generalization of the sine and cosine of the phase shifts in the usual scattering theory for a spherical symmetric potential.[17])

Now, one might naturally ask, what happens if we introduce in the rhs of Eqs. (A9) and (A12) the t matrix of a unit-cell potential which is not of muffin-tin type? Clearly, the fact that the series Eq. (A6) converges[28] only for $|\boldsymbol{\rho}-\boldsymbol{\rho}'| \leq |\mathbf{R}-\mathbf{R}'|$, doesn't make apparent that the series Eqs. (A9)–(A12) is divergent where the t matrix now corresponds to a non-muffin-tin potential. However, even if these series are convergent, they apparently do not represent the matrix elements, Eq. (20), of the operators defined in Eq. (5) because, in the non-muffin-tin case, the decomposition of the Green function changes its functional form from point to point [in contradistinction to Eq. (A6)].[28] [Some authors[9] consider, however, that such series represent, as an exact result, the matrix elements, Eq. (20).]

---

[1] E. Wimmer, H. Krakauer, M. Weinert, and A. J. Freeman, Phys. Rev. B **24**, 864 (1981).

[2] J Korringa, Physica **XIII**, 392 (1947); W. Kohn and N. Rostoker, Phys. Rev. **94**, 1111 (1954).

[3] J. L. Beeby, Proc. Ry. Soc. London A **302**, 113 (1967).

[4] D. Soven, Phys. Rev. **156**, 809 (1967).

[5] G. M. Stocks, W. M. Temmerman, and B. L. Gyorffy, Phys. Rev. Lett. **41**, 339 (1978).

[6] J. S. Faulkner and G. M. Stocks, Phys. Rev. B **21**, 3222 (1980).

[7] F. Calogero, *Variable Phase Approach to Potential Scattering* (Academic, New York, 1967), and references therein.

[8] More efficient schemes of computation can be found in C. Dullemond *et al.*, Comput. Phys. Commun. **27**, 377 (1982) and V. Rokhlin, J. of Comput. Phys. **60**, 187 (1985).

[9] R. G. Brown and M. Ciftan, Phys. Rev. B **27**, 4564 (1983); **32**, 1343 (1985); **33**, 7937 (1986).

[10] A. Gonis, Phys. Rev. B **33**, 5914 (1986).

[11] S. Nagano and S. Y. Tong, Phys. Rev. B **32**, 6562 (1985).

[12] J. S. Faulkner, Phys. Rev. B **32**, 1339 (1985); **34**, 5931 (1986).

[13] B. L. Gyorffy and G. M. Stocks, *Electrons in Disordered Metals and at Metallic Surfaces* (Plenum, New York, 1979).

[14] P. Lloyd and P. V. Smith, Adv. Phys. **21**, 69 (1972).

[15] R. K. Nesbet, Phys. Rev. B **30**, 4230 (1984); **33**, 8027 (1986).

[16] E. Badralexe and A. J. Freeman, preceding paper, Phys. Rev. B **36**, 1378 (1987).

[17] M. Reed and B. Simmon, *Methods of Modern Mathematical*

Physics (Academic, New York, 1978).

[18] Hereafter we discuss only the case of positive energy, $E \geq 0$. For negative energy, $E < 0$, we should replace the kernel of the Green function in Eq. (6) according to $e^{\pm i\sqrt{E}\,|r-r'|} \rightarrow e^{-\sqrt{E}\,|r-r'|}$. This results in changing $\sqrt{E} \rightarrow \pm i\sqrt{-E}$ and $\pm i n_L \rightarrow i n_L$, everywhere.

[19] J. Callaway, *Quantum Theory of the Solid State* (Academic, New York, 1974).

[20] One cannot take directly the lattice Fourier transform of Eq. (5) because its existence is not apparent, i.e., the $\mathbf{R}-\mathbf{R}'$ dependence of the kernels in Eq. (5) is not obvious. However, suppose we know (by other means) the existence of this property, then the direct calculation of the lattice Fourier transform of Eq. (5) yields immediately the relations given by Eqs. (10) and (13). In the muffin-tin case (see Appendix) this point is greatly simplified by the decomposition of the Green function between two adjacent muffin-tins and by the use of the Born series expressed with the muffin-tin t matrix (Refs. 3 and 13) and not of Eq. (7).

[21] H. Holden, R. Hoegh-Krohn, and M. Mebkhout, J. Math. Phys. **26**, 145 (1985), and references therein.

[22] To save space, we confine ourselves here only to the on-shell matrix elements. The partial off-shell matrix elements

$$\int\int j_L^*(E,r)T^{\pm}(E,\mathbf{r},\mathbf{r}')j_{L'}(E',\mathbf{r}')d\mathbf{r}\,d\mathbf{r}'$$

can be calculated similarly but the total off-shell matrix elements require much effort.

[23] M. Danos and L. C. Maximon, J. Math. Phys. **6**, 766 (1964).

[24] In fact, any function $f(\mathbf{r})$ which is square integrable (even in a generalized sense) can be shown to satisfy the relation

$$\int \frac{d\boldsymbol{\kappa}}{\tilde{\omega}} \int_{\Omega} f^*(\boldsymbol{\kappa},\boldsymbol{\rho})f(\boldsymbol{\kappa},\boldsymbol{\rho})d\boldsymbol{\rho} = \int_{R^3} f^*(\mathbf{r})f(\mathbf{r})d\mathbf{r}\ ,$$

where $f(\boldsymbol{\kappa},\boldsymbol{\rho})$ is obtained by the folding procedure Eqs. (24) or (25). More details about these properties can be found in Ref. 17.

[25] In fact, that is to manipulate the relation

$$\delta(\mathbf{r}-\mathbf{r}') = \frac{\delta(r-r')}{r^2}\delta(\hat{\mathbf{r}}-\hat{\mathbf{r}}') = \frac{\delta(r-r')}{r^2}\sum_L Y_L^*(\hat{\mathbf{r}})Y_L(\hat{\mathbf{r}}')$$

[compare the **K** expansions in Eqs. (27) and (35)]. Alternatively, one can use the expansion of the plane wave in spherical waves

$$\frac{e^{\pm i\mathbf{p}\mathbf{r}}}{(2\pi)^{3/2}} = \sum_L (\pm i)^l Y_L^*(\hat{\mathbf{p}})j_L(p^2,\mathbf{r})\ .$$

[26] A detailed exposition of this point and of the way to circumvent it for the case of the eigenvalue equation was recently given in Ref. 16.

[27] Because the kernel of the Green function in Eq. (46) is defined in the Hilbert space of Bloch-periodic functions, this definition should be kept for Eq. (50) and similarly for Eq. (38). In fact, the point here is to properly describe the Bloch function in Eq. (50) in terms of coefficients $A_L^{\pm}(\boldsymbol{\kappa},E)$. A detailed discussion of this point can be found in Ref. 16.

[28] One can easily see that Eq. (A6) holds only for those points which satisfy the relation $|\boldsymbol{\rho}-\boldsymbol{\rho}'| \leq |\mathbf{R}-\mathbf{R}'|$. Actually, if this condition is not satisfied, then Eq. (A6) contradicts Eq. (6). Obviously, the above condition is always satisfied by cells far enough and the only trouble with the decomposition Eq. (A6) appears in the case of next neighbors. For example, if at least one point $\boldsymbol{\rho}$ or $\boldsymbol{\rho}'$, say $\boldsymbol{\rho}$, is outside of the inscribed sphere then we have either the decomposition Eq. (A6) if $|\boldsymbol{\rho}-\boldsymbol{\rho}'| \leq |\mathbf{R}-\mathbf{R}'|$, or the decomposition

$$G^{\pm}(E,\mathbf{R}+\boldsymbol{\rho},\mathbf{R}'+\boldsymbol{\rho}') = \frac{\mp i\pi\sqrt{E}}{2}\sum_L j_L(E,\boldsymbol{\rho})\left[\sum_{L'} H_{LL'}^{\pm}(E,\mathbf{R}-\mathbf{R}')j_{L'}^*(E,\boldsymbol{\rho}')\right]$$

if $\rho \leq |\mathbf{R}'-\mathbf{R}+\boldsymbol{\rho}'|$, or the decomposition

$$G^{\pm}(E,\mathbf{R}+\boldsymbol{\rho},\mathbf{R}'+\boldsymbol{\rho}') = \frac{\mp i\pi\sqrt{E}}{2}\sum_L h_L^{\pm}(E,\boldsymbol{\rho})\left[\sum_{L'} J_{LL'}(E,\mathbf{R}-\mathbf{R}')j_{L'}^*(E,\boldsymbol{\rho}')\right]$$

if $\rho > |\mathbf{R}'-\mathbf{R}+\boldsymbol{\rho}'|$. Notice then the appearance of a prescribed order in performing the sums as well as the change of the functional form from point to point, in contradistinction to Eq. (A6). Clearly, these two features make Eq. (A1) useless in the exact treatment of a non-muffin-tin potential (Refs. 11 and 13). In fact, this was the reason we developed an approach here based on Eq. (7) and not on the well known Eq. (A1).

[29] A. Lodder, J. Phys. F **10**, 1117 (1980).

[30] Strictly speaking, Eq. (A1) holds only for perturbative potentials as it is always derived (e.g., Refs. 3 and 13) by means of the Born series. However, in view of Eqs. (5)–(13) in the present paper one can see that the final results, Eqs. (A9) and (A12), remain true whether the potential is perturbative or not.