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

Energy-band equation for a general periodic potential

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

(Received 10 November 1986)

A new approach—one not based on multiple scattering or the variational principle—to the problem of the band structure for a general (i.e., non-muffin-tin) periodic potential is presented. From the eigenvalue equation, the Bloch function is shown to be expandable as a multipole series around the origin and the coefficients are found to be given as functionals of the Bloch function and the cell potential. By introducing into this functional various representations of the Bloch function (as a superposition in which each individual term *is not* Bloch periodic), we obtain previously derived band-structure equations (some claimed to be exact). By deriving, however, a new representation for the Bloch function (as an on-shell superposition in which each term *is* Bloch periodic) and using this representation in the above functional, we obtain a new energy-band equation in which the potential can no longer be separated from the structure. When approximations are introduced, then Korringa-Kohn-Rostoker-type equations (in which the potential is separated from the structure) may be obtained. All the steps of this new approach are illustrated in the soluble case of a constant periodic potential. It is shown, in this case, that only the newly introduced band-structure equation is able to generate the correct eigenvalues.

I. INTRODUCTION

The early and continuing success of the Korringa, Kohn, and Rostoker[1] (KKR) approach to solving a variety of problems for ordered and disordered solids has fostered many attempts at generalizing their treatment to the case of a general (i.e., non-muffin-tin) potential.[2–6] In the case of a muffin-tin potential, it is universally accepted that the structure gets separated from the potential and the eigenvalues are given by the KKR equation—a result that makes possible highly efficient band-structure calculations. In the case of a non-muffin-tin, i.e., general periodic potential, the structure is no longer separated from the potential and the so-called "near-field correction" should be taken into account.[7] These corrections, however, although different from zero,[7] are usually neglected; also, except for an upper bound (determined by neglecting them and comparing the result so obtained with the exact one in a soluble case[7]), neither practical evaluations were done, nor was any soluble case studied.

In contradiction to the general view,[2,5–7] two references[3,4] conclude that in the case of closed-packed lattices, the band-structure equation for a general potential acquires the same functional form as the usual KKR equation. That is, the structure gets separated from the potential as an *exact* result, and the effect of the structure is fully described by means of the usual structure constant as defined in the KKR equation. However, although Refs. 3 and 4 agree upon the separation between structure and potential, they strongly disagree on the analytical form of the potential contribution. Moreover, although they contain quite different potential contributions, the equations of Refs. 3 and 4 yield the same results for the empty lattice test. Further, these results are systematically shifted from the correct ones (in the sense that the error can not be decreased by systematically increasing the L space).[7,3] This striking feature, i.e., different equations which yield the same results and which are systematically shifted from the correct ones, appears to suggest that the equations in both Refs. 3 and 4, although claimed as exact results, reflect solely the same (hidden) approximation. In this paper, we show that this, in fact, is the case. Finally, the band-structure equations given in Refs. 3 and 4 have neither been proved (analytically) to yield the result as obtained by the plane-wave diagonalization (which represents the exact result) nor were they solved (analytically) in a particular (but relevant, full potential) case. We agree, therefore, with the conclusion of Faulkner[7] that the existence of a KKR-type (or, more generally, L representation) band-structure equation for a general periodic potential still remains an open problem.

The present paper considers this problem using a completely different approach from those employed so far, i.e., multiple scattering and variational principle. Our philosophy can be summarized as follows: if there were a KKR-type equation for a general potential, it ought to be derived from the eigenvalue equation of the Bloch function by means of a proper analysis (since the eigenvalue equation contains all the necessary information). Here, we present such an analysis.[8] From the eigenvalue equation we infer that the Bloch function can be expanded around the origin in a multipole series whose coefficients are expressed as functionals of the Bloch function and the cell potential. From this boundary condition and, again, from the eigenvalue equation, we further derive that the Bloch function extended (with Bloch boundary conditions) to an arbitrary sphere can be written as a superposition of the regular solutions of the (periodic) potential enclosed by that sphere. This, in turn, is shown to result (by using a folding procedure) in representing the Bloch function as an on-shell superposition of Bloch periodic orbitals. It is emphasized (by comparing with other representations) that only the above superposition of Bloch periodic orbitals correctly describes the Bloch function (as an element of the Hilbert space of Bloch periodic functions). Finally, by introducing the Bloch function as given by various representations in the functional defining the multipole expansion around the origin, we find the band-structure equation previously derived.[3,4] More significantly, we also obtain a new band-structure equation which, in contradistinction with previous ones, contains the newly introduced "multipole expansion periodicity corrections." The contribution brought about by these corrections is illustrated in a soluble case: for a constant periodic potential, only the newly derived KKR-type band equation is able to reproduce the correct result.

II. MULTIPOLE EXPANSIONS AND BAND-STRUCTURE EQUATIONS

Let $\mathbf{R}$ and $\mathbf{K}$ be vectors of the direct and reciprocal lattices, having the primitive cells Ω and $\tilde{\Omega}$, with the volume ω and $\tilde{\omega}$, respectively. 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 $\mathbf{r}$ and $\mathbf{k}$, in the whole space, according to the Fig. 1, there is a unique decomposition

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

Let $V(\mathbf{r})$, 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 the potential $\mathcal{V}_{\mathbf{R}}$ is zero outside the cell indexed by $\mathbf{R}$, i.e.,

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

and the cell potential $\mathcal{V}(\boldsymbol{\rho})$ has the range α, $\alpha\leq\max_{\rho\in\Omega}\rho$ where ρ denotes the modulus $|\boldsymbol{\rho}|$ (hereafter, r will denote the modulus $|\mathbf{r}|$). In this notation, the muffin-tin (MT) 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, $d\geq 0$, we introduce the potential $V^d(\mathbf{r})$, as defined by

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

where $V(\mathbf{r})$ is defined in Eq. (2). Obviously, $V^\mu=\mathcal{V}^{\mathrm{MT}}$ denotes the cell potential restricted to the inscribed sphere (and zero elsewhere).

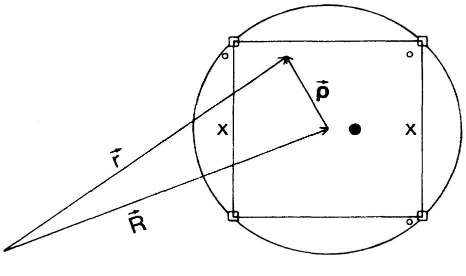

FIG. 1. Coordinate representation.

In this notation, the Bloch function $\Psi(\boldsymbol{\kappa},E_n,\boldsymbol{\rho})$, $\boldsymbol{\kappa}\in\tilde{\Omega}$, and $\boldsymbol{\rho}\in\Omega$ with the energy $E_n(\boldsymbol{\kappa})>0$, being an element of the Hilbert space $\mathcal{H}(\boldsymbol{\kappa})$ spanned by the plane waves $(e^{i(\boldsymbol{\kappa}+\mathbf{K})\rho}/\sqrt{\omega})_{\mathbf{K}}$, is defined as solution of the eigenvalue integral equation[9]

$$\Psi(\boldsymbol{\kappa},E,\boldsymbol{\rho})=\int_\Omega\sum_{\mathbf{R}}e^{i\boldsymbol{\kappa}\cdot\mathbf{R}}\left(\frac{-1}{4\pi}\right)\frac{\cos(\sqrt{E}\,|\boldsymbol{\rho}-\mathbf{R}-\boldsymbol{\rho}'|)}{|\boldsymbol{\rho}-\mathbf{R}-\boldsymbol{\rho}'|}\times\mathcal{V}(\boldsymbol{\rho}')\Psi(\boldsymbol{\kappa},E,\boldsymbol{\rho}')d\boldsymbol{\rho}'\ ,\tag{5}$$

where the (principal value) Green function has the following (multipole) decomposition

$$\left(\frac{-1}{4\pi}\right)\frac{\cos(\sqrt{E}\,|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|}=\frac{\pi\sqrt{E}}{2}\sum_L j_L(E,\mathbf{r}_<)n_L^*(E,\mathbf{r}_>)\tag{6}$$

where $|\mathbf{r}_<|=\min(r,r')$, $|\mathbf{r}_>|=\max(r,r')$, and $L=(l,m)$ and, as usual, the Bessel (j_L) and Neumann (n_L) functions are products of the spherical Bessel and Neumann functions and spherical harmonics.

Now, by using in Eqs. (5) and (6) the behavior of the Bessel and Neumann functions at the origin, we find the following boundary condition

$$\Psi(\boldsymbol{\kappa},E_n,\boldsymbol{\rho})\to\sum_L j_L(E_n(\boldsymbol{\kappa}),\boldsymbol{\rho})A_L(\boldsymbol{\kappa},E_n)\ \text{as}\ \boldsymbol{\rho}\to\mathbf{0}\ ,\tag{7}$$

where we introduced the abbreviations

$$A_L(\boldsymbol{\kappa},E_n)=\frac{\pi\sqrt{E_n}(\boldsymbol{\kappa})}{2}\int_\Omega n_L^*(\boldsymbol{\kappa},E_n(\boldsymbol{\kappa}),\boldsymbol{\rho})\times\mathcal{V}(\boldsymbol{\rho})\Psi(\boldsymbol{\kappa},E_n,\boldsymbol{\rho})d\boldsymbol{\rho}\ ,\tag{8}$$

$$n_L(\boldsymbol{\kappa},E,\boldsymbol{\rho})=n_L(E,\boldsymbol{\rho})+\mathrm{n}_L(\boldsymbol{\kappa},E,\boldsymbol{\rho})\ ,\tag{9a}$$

$$\mathrm{n}_L(\boldsymbol{\kappa},E,\boldsymbol{\rho})=\sum_{\mathbf{R}\neq 0}e^{-i\boldsymbol{\kappa}\cdot\mathbf{R}}n_L(E,\boldsymbol{\rho}+\mathbf{R})\ .\tag{9b}$$

As the (Bloch periodic) Green function in Eq. (5) is defined only when acting in the Hilbert space $\mathcal{H}(\boldsymbol{\kappa})$ of Bloch periodic functions, it follows that the integral in the right-hand side (rhs) of Eq. (8) is defined only for Ψ being a Bloch function. For later use, we mention the relation

$$\int_\Omega n_L^*(\boldsymbol{\kappa},E,\boldsymbol{\rho})e^{i(\boldsymbol{\kappa}+\mathbf{K})\cdot\rho}d\boldsymbol{\rho}=\frac{(2\pi)^{3/2}i^lY_L^*(\hat{\mathcal{K}})}{E-(\boldsymbol{\kappa}+\mathbf{K})^2}\frac{2}{\pi\sqrt{E}}\left(\frac{(\boldsymbol{\kappa}+\mathbf{K})^2}{E}\right)^{l/2}\ ,\tag{10}$$

where $\mathcal{K}=\boldsymbol{\kappa}+\mathbf{K}$, which is obtained by considering the action of the Green function that appears in Eq. (5) upon the plane wave, using the plane-wave expansion of this (Bloch periodic) Green function and taking the multipole expansion in the limit $\boldsymbol{\rho}=\mathbf{0}$. The function $n_L(\boldsymbol{\kappa},E,\boldsymbol{\rho})$ defined in Eq. (9) contains information concerning only the geometry of the lattice; for $\rho \leq \min R$, it can be represented as

$$n_L(\boldsymbol{\kappa},E,\boldsymbol{\rho})=n_L(E,\boldsymbol{\rho})+\sum_{L'} j_{L'}(E,\boldsymbol{\rho})N_{L'L}(\boldsymbol{\kappa},E) \ ,$$
$$\rho \leq \min R \ , \tag{11}$$

where $N_{LL'}(\boldsymbol{\kappa},E)$ is the usual structure constant.[1] For those ρ with $\rho \geq \min R$, the sum in Eq. (11) is not convergent;[10] however, we can isolate in Eq. (9) a finite number of terms with $R \leq \rho$, i.e., the nearest neighbors, and obtain for the remaining (infinite) sum an expression similar to the last term in Eq. (11).

Equation (8) represents the crucial point of our investigation: Provided that the Bloch function can be represented as a superposition having the coefficients $A_L(\boldsymbol{\kappa},E_n)$, then Eq. (8) allows us to transform the (integral) eigenvalue problem, Eq. (5), into an (algebraic) homogeneous linear system for these coefficients. Thus, the point is now to describe correctly the Bloch function [i.e., as an element of the Hilbert space $\mathcal{H}(\boldsymbol{\kappa})$] in terms of coefficients $A_L(\boldsymbol{\kappa},E_n)$ defined by the boundary condition, Eq. (7). Surely, such a description can be inferred only from Eq. (5), as this (eigenvalue) equation contains all the relevant information concerning the Bloch function. Hence, we now focus on this equation.

Since, from Eqs. (5) and (6), the Bloch function admits a multipole expansion inside the inscribed sphere and this expansion is unique, we have for $\rho \leq \mu$

$$\Psi(\boldsymbol{\kappa},E_n,\boldsymbol{\rho})=\sum_L \Phi_L^{\mathrm{MT}}(E_n(\boldsymbol{\kappa}),\boldsymbol{\rho})A_L(\boldsymbol{\kappa},E_n), \quad \rho \leq \mu \tag{12}$$

where the functions $\Phi_L^{\mathrm{MT}}(E_n(\mathbf{x}),\boldsymbol{\rho})$ are solutions of the (partial differential) equation

$$(\Delta+E)\Phi_L^{\mathrm{MT}}(E,\boldsymbol{\rho})=\mathcal{V}^{\mathrm{MT}}(\rho)\Phi_L^{\mathrm{MT}}(E,\boldsymbol{\rho}) \tag{13}$$

at the energy $E=E_n(\boldsymbol{\kappa})$ and with boundary conditions

$$\Phi_L^{\mathrm{MT}}(E,\boldsymbol{\rho})\rightarrow j_L(E,\boldsymbol{\rho}) \text{ as } \boldsymbol{\rho}\rightarrow \mathbf{0} \ . \tag{14}$$

Now, for reasons to be obvious later, we want to extend the multipole expansion description beyond the inscribed sphere. Thus, we introduce the function $\Psi^d(\boldsymbol{\kappa},E_n,\mathbf{r})$ defined for $r=|\boldsymbol{\rho}+\mathbf{R}|\leq d$ and for any finite $d \geq 0$, as the prolongation[11] of the Bloch function with Bloch boundary conditions

$$\Psi^d(\boldsymbol{\kappa},E_n,\boldsymbol{\rho}+\mathbf{R})=e^{i\boldsymbol{\kappa}\cdot\mathbf{R}}\Psi(\boldsymbol{\kappa},E_n,\boldsymbol{\rho}) \ , \tag{15a}$$

$$\nabla\Psi^d(\boldsymbol{\kappa},E_n,\boldsymbol{\rho}+\mathbf{R})=e^{i\boldsymbol{\kappa}\cdot\mathbf{R}}\nabla\Psi(\boldsymbol{\kappa},E_n,\boldsymbol{\rho}) \ . \tag{15b}$$

The function $\Psi^d(\boldsymbol{\kappa},E_n,\mathbf{r})$ is then given by the rhs of Eq. (5) with $\boldsymbol{\rho}\rightarrow\mathbf{r}$ and $E\rightarrow E_n$ and hence

$$\Psi^d(\boldsymbol{\kappa},E_n,\mathbf{r})=\sum_L Y_L(\hat{\mathbf{r}})\psi_L^d(\boldsymbol{\kappa},E_n,r), \quad r \leq d \tag{16}$$

where use was made of Eq. (6). Further, we find that the functions $\psi_L^d(\boldsymbol{\kappa},E_n,r)$ can be related to the multipole components $\phi_{L'L}^{d,\lambda}(E,r)$ of the functions

$$\Phi_L^{d,\lambda}(E,\mathbf{r})=\sum_{L'} Y_{L'}(\hat{\mathbf{r}})\phi_{L'L}^{d,\lambda}(E,r) \tag{17}$$

which are defined by[12]

$$\begin{gathered}(\Delta+E)\Phi_L^{d,\lambda}(E,\mathbf{r})=V^d(\mathbf{r})\Phi_L^{d,\lambda}(E,\mathbf{r}) \ , \\ \Phi_L^{d,\lambda}(E,\mathbf{r})\rightarrow\lambda_L(E,\mathbf{r}) \text{ as } r\rightarrow d \ ,\end{gathered} \tag{18}$$

at $E=E_n(\boldsymbol{\kappa})$ and where λ stands for either Bessel function j or Neumann function n. Actually, by taking $\boldsymbol{\rho}\rightarrow\mathbf{r}$ in Eq. (5), commuting a finite subsum with the integral and using Eq. (6), we obtain

$$\psi_{L'}^d(\boldsymbol{\kappa},E_n,r)=\sum_L [\phi_{L'L}^{d,j}(E_n(\boldsymbol{\kappa}),r)B_L^d + \phi_{L'L}^{d,n}(E_n(\boldsymbol{\kappa}),r)C_L^d] \ , \tag{19}$$

where B and C [whose dependence on $\boldsymbol{\kappa}$ and $E_n(\boldsymbol{\kappa})$ was omitted] are given at $E=E_n(\boldsymbol{\kappa})$ by

$$\begin{gathered}B_L^d=A_L(\boldsymbol{\kappa},E)-\frac{\pi\sqrt{E}}{2}\int_{r\leq d} n_L^*(E,\mathbf{r})V^d(\mathbf{r})\Psi^d(\boldsymbol{\kappa},E,\mathbf{r})d\mathbf{r} \ , \\ C_L^d=\frac{\pi\sqrt{E}}{2}\int_{r\leq d} j_L^*(E,\mathbf{r})V^d(\mathbf{r})\Psi^d(\boldsymbol{\kappa},E,\mathbf{r})d\mathbf{r} \ .\end{gathered} \tag{20}$$

If one now uses Eqs. (19) and (8) in Eq. (20), and after some algebra involving the theory of the variable-phase method,[12] we conclude that for any $r \leq d$, i.e., not only for $r \leq \mu$, the function $\Psi^d(\boldsymbol{\kappa},E_n,\mathbf{r})$ is given by

$$\Psi^d(\boldsymbol{\kappa},E_n,\mathbf{r})=\sum_L \Phi_L^d(E_n(\boldsymbol{\kappa}),\mathbf{r})A_L(\boldsymbol{\kappa},E_n), \quad r \leq d \ . \tag{21}$$

Here the functions $\Phi_L^d(E_n(\boldsymbol{\kappa}),\mathbf{r})$ are the regular solutions

$$\begin{gathered}(\Delta+E)\Phi_L^d(E,\mathbf{r})=V^d(\mathbf{r})\Phi_L^d(E,\mathbf{r}) \ , \\ \Phi_L^d(E,\mathbf{r})\rightarrow j_L(E,\mathbf{r}) \text{ as } \mathbf{r}\rightarrow\mathbf{0} \ ,\end{gathered} \tag{22a}$$

taken at the energy $E=E_n(\boldsymbol{\kappa})$; they have, for $r \leq \min(d,d')$, the obvious property

$$\Phi_L^d(E,\mathbf{r}=\Phi_L^{d'}(E,\mathbf{r}), \quad r \leq \min(d,d') \ . \tag{22b}$$

The coefficients $A_L(\boldsymbol{\kappa},E_n)$ are independent of d and coincide with those defined in Eq. (8) and used in Eq. (12). [In fact,[11] this was the reason for introducing the prolongation defined by Eq. (15).] Equation (21) says that the function $\Psi^d(\boldsymbol{\kappa},E_n,\mathbf{r})$, which coincides with the Bloch function only inside the sphere $r \leq d$, can be represented as a superposition of the functions $\Phi_L^d(E_n,\mathbf{r})$ given in Eq. (22a). Inside the unit cell, the functions $\Phi_L^d(E,\mathbf{r})$ satisfy the Schrödinger equation with the cell potential but only as a (partial) differential equation. That is, irrespective of the energy E, these functions are not Bloch periodic; later, in Sec. IV, we will see such an example: Each term is not Bloch periodic but their sum belongs to the space of Bloch periodic functions.[13] Obviously, the restriction of Eq. (21) for $\mathbf{r}=\boldsymbol{\rho}\in\Omega$ gives the values of the Bloch function inside the unit cell

$$\Psi(\boldsymbol{\kappa},E_n,\boldsymbol{\rho})=\sum_L \Phi_L^d(E_n(\boldsymbol{\kappa}),\boldsymbol{\rho})A_L(\boldsymbol{\kappa},E_n) \tag{23a}$$

which, in view of Eq. (22b), requires the regular solution of Eq. (22a) only for the case where d is equal to the radius of the circumscribing sphere, hereafter denoted by $\Phi_L^{\text{circ}}(E,\boldsymbol{\rho})$

$$\Psi(\boldsymbol{\kappa},E_n,\boldsymbol{\rho})=\sum_L \Phi_L^{\text{circ}}(E_n(\boldsymbol{\kappa}),\boldsymbol{\rho})A_L(\boldsymbol{\kappa},E_n) \ . \tag{23b}$$

However, this is not the multipole expansion of the Bloch function (which, in fact, does not exist) but rather (the restriction) of one of its prolongations.[11] The interesting point about Eq. (23b) is the fact that each term is not Bloch periodic but their sum represents a Bloch periodic function (again, we will see an example in Sec. IV). This suggests a very careful treatment of the A_L coefficients. Actually, let us suppose that a Bloch energy $E_n(\boldsymbol{\kappa})$ is given, and hence that the functions $\Phi_L^d(E_n(\mathbf{x}),\mathbf{r})$, as solution of Eq. (22a), are known, but the corresponding Bloch function is not known; then, how should the A_L coefficients be chosen in order that the sum in Eq. (23b), where each individual term is not Bloch periodic, will represent a Bloch periodic function? In this respect, is it sufficient to consider only the system of equations obtained by introducing Eq. (23b) in Eq. (8) or do we have to consider additional equations [e.g., obtained by introducing Eq. (21) into Eq. (15)] in order to correctly describe the Bloch periodicity? Clearly, it would be more convenient to convert Eq. (23) into a representation in which each individual term is Bloch periodic in which case the periodicity conditions, Eq. (15), are identically satisfied. We now focus on this problem.

Coming back to Eq. (21), we notice that in the limit $d=\infty$, it gives the multipole expansion of the Bloch function extended [with Bloch boundary conditions, Eq. (15)] in the whole space. Then, the Bloch function inside the unit cell can be obtained by folding back the prolongation, Eq. (21), for $d=\infty$. More precisely, an alternative form of Eq. (23) is provided by the observation that for each point $\boldsymbol{\rho}\in\Omega$, there is a finite number $n^d(\boldsymbol{\rho})$ of translations $\mathbf{R}$ that leaves this point inside the sphere with radius d. For example, in Fig. 1 we refer to the case d as the radius of the circumscribing sphere; in this case, $n^d(\boldsymbol{\rho})$ can take the value 4 (e.g., the points denoted as □), or the value 3 (denoted as ○), or the value 2 (denoted as ×) or the value 1 (denoted as ●). For the case d as fixed, $n^d(\boldsymbol{\rho})$ is a piecewise constant function, monotonically increasing with d, and having the properties

$$\begin{gathered} n^d(\boldsymbol{\rho}+\mathbf{R})=n^d(\boldsymbol{\rho}) \quad \text{for } |\boldsymbol{\rho}+\mathbf{R}|\leq d \ , \\ n^{\mu}(\boldsymbol{\rho})=1 \ , \\ \lim_{d\to\infty} n^d(\boldsymbol{\rho})=N_\Omega^d=N_\Omega\to\infty \ . \end{gathered} \tag{24}$$

By now using Eq. (15a) in Eq. (21) for each $\mathbf{R}$ with $|\mathbf{r}+\mathbf{R}|\leq d$ [whose number is given by $n^d(\mathbf{r})$], Eq. (23) can be written as

$$\Psi(\boldsymbol{\kappa},E_n,\mathbf{r})=\sum_L \widetilde{\Phi}{}_L^d(\boldsymbol{\kappa},E_n(\boldsymbol{\kappa}),\mathbf{r})A_L(\boldsymbol{\kappa},E_n) \ , \tag{25a}$$

$$\Psi(\boldsymbol{\kappa},E_n,\boldsymbol{\rho})=\sum_L \widetilde{\Phi}{}_L^d(\boldsymbol{\kappa},E_n(\boldsymbol{\kappa}),\boldsymbol{\rho})A_L(\boldsymbol{\kappa},E_n) \ , \tag{25b}$$

where we introduced the notation

$$\widetilde{\Phi}{}_L^d(\boldsymbol{\kappa},E,\boldsymbol{\rho})=\frac{1}{n^d(\boldsymbol{\rho})}\Phi_L^d(\boldsymbol{\kappa},E,\boldsymbol{\rho}) \ , \tag{26a}$$

$$\Phi_L^d(\boldsymbol{\kappa},E,\boldsymbol{\rho})=\sum_{\mathbf{R},\,|\boldsymbol{\rho}+\mathbf{R}|\leq d} e^{-i\boldsymbol{\kappa}\cdot\mathbf{R}}\Phi_L^d(E,\boldsymbol{\rho}+\mathbf{R}) \tag{26b}$$

at $E=E_n(\boldsymbol{\kappa})$. Equation (25) represents an attempt to transform the rhs of Eq. (23a) into a superposition in the Hilbert space of Bloch functions denoted above by $\mathcal{H}(\boldsymbol{\kappa})$. Actually, the functions $\widetilde{\Phi}{}_L^d(\boldsymbol{\kappa},E,\boldsymbol{\rho})$ (at any E) satisfy Eq. (15a) but they are discontinuous at those points at which the function $n^d(\boldsymbol{\rho})$ changes its value [recall that $n^d(\boldsymbol{\rho})$, Eq. (24), represents a piecewise constant function]. Thus, the rhs of Eq. (25) is not (yet) a superposition of Bloch periodic functions, but for any required accuracy one can find a d for which the functions $\widetilde{\Phi}{}_L^d(\boldsymbol{\kappa},E,\boldsymbol{\rho})$ become continuous. Thus, in the limit $d=\infty$, the functions $\widetilde{\Phi}{}_L^d(\boldsymbol{\kappa},E,\boldsymbol{\rho})$ satisfy, irrespective of E, both Eqs. (15a) and (15b), and hence,[14] Eq. (25) becomes a superposition in the Hilbert space $\mathcal{H}(\boldsymbol{\kappa})$. Then, the difference between Eqs. (23) and (25) pertains to the description of the Bloch function as a superposition of Bloch periodic functions, i.e., as a superposition in the space $\mathcal{H}(\boldsymbol{\kappa})$. Obviously, Eq. (25) satisfies identically the periodicity conditions, Eq. (15). Hence, the A_L coefficients in Eq. (25) can no longer be subject to any condition except Eq. (8) which then uniquely specifies the Bloch function. In this sense, the A_L coefficients of Eq. (25) are on the same footing as the coefficients of the (Bloch periodic) plane-wave expansion of the Bloch function (in which each individual term is Bloch periodic and the coefficients are required to only satisfy the Schrödinger equation. Notice, however, that Eq. (25) has an on-shell character whereas in the plane-wave expansion each term does not satisfy the Schrödinger equation with the cell potential. More than that, on the basis of the existence of a multipole expansion,[11] one can combine Eqs. (23b) and (25b) to obtain the representation

$$\Psi(\boldsymbol{\kappa},E_n,\boldsymbol{\rho})=\sum_L \begin{cases} \Phi_L^{\text{MT}}(E_n(\boldsymbol{\kappa}),\boldsymbol{\rho})A_L(\boldsymbol{\kappa},E_n) & \text{for } \rho\leq\mu \\ \widetilde{\Phi}{}_L^d(\boldsymbol{\kappa},E_n(\boldsymbol{\kappa}),\rho)A_L(\boldsymbol{\kappa},E_n) & \text{for } \boldsymbol{\rho}\in\Omega,\ \rho\geq\mu \end{cases} \tag{26c}$$

where the A_L coefficients are restricted by the continuity condition of the Bloch function and its derivative on the surface of the inscribed sphere. Equation (26c) rephrases the old idea[15] of representing the Bloch function as a multipole expansion within the inscribed sphere as a superposition of plane waves in the rest of the unit cell

$$\Psi(\boldsymbol{\kappa},E_n,\boldsymbol{\rho})=\begin{cases} \sum_L \Phi_L^{\text{MT}}(E_n(\boldsymbol{\kappa}),\boldsymbol{\rho})A_L(\boldsymbol{\kappa},E_n) & \text{for } \rho\leq\mu \\ \sum_{\mathbf{K}} \dfrac{e^{i(\boldsymbol{\rho}+\mathbf{K})\cdot\boldsymbol{\rho}}}{\sqrt{\omega}}a_{\mathbf{K}}(E_n) & \text{for } \boldsymbol{\rho}\in\Omega,\ \rho\geq\mu \end{cases} \tag{26d}$$

where the two sets of coefficients are connected by a matching condition (both the function and its derivative on the surface of the inscribed sphere). By comparing

Eqs. (26c) and (26d), we notice a clear advantage concerning the interstitial region: Each term in Eq. (26c) satisfies the Schrödinger equation and, moreover, satisfies Eq. (15a) as well, whereas in Eq. (26d) we need many plane waves to satisfy correctly the Schrödinger equation. There is also a disadvantage, namely Eq. (15b) is satisfied only in the limit $d=\infty$ whereas Eq. (26d) is always Bloch periodic. However, as the band structure based on Eq. (23), i.e., based on taking only the term $R=0$ in Eq. (26b), already gives a fairly accurate result,[7,3] we may expect that taking all the terms in Eq. (26b) for a small d, say the radius of the circumscribing sphere, will do the job of many plane waves in Eq. (26d). Hereafter, it will be convenient to separate the $\boldsymbol{\kappa}$ dependence in Eq. (26) [and hence in Eq. (25)] as given by

$$\begin{aligned}\tilde{\Phi}^{d}_{L}(\boldsymbol{\kappa},\mathbf{E},\boldsymbol{\rho})&=\Phi^{\text{circ}}_{L}(E,\boldsymbol{\rho})+\varphi^{d}_{L}(\boldsymbol{\kappa},E,\boldsymbol{\rho})\ ,\\ \varphi^{d}_{L}(\boldsymbol{\kappa},E,\boldsymbol{\rho})&=\frac{1}{n^{d}(\boldsymbol{\rho})}\sum_{\mathbf{R}\neq 0,\ |\rho+R|\leq d}[e^{-i\boldsymbol{\kappa}\cdot\mathbf{R}}\Phi^{d}_{L}(E,\boldsymbol{\rho}+\mathbf{R})\\ &\qquad -\Phi^{\text{circ}}_{L}(E,\boldsymbol{\rho})]\ .\end{aligned} \tag{26e}$$

Now, since we have expressed the Bloch function as a superposition with coefficients $A_L(\boldsymbol{\kappa},E_n)$, we come back to Eq. (8) with the hope, as already stated, of establishing a homogeneous linear system for these coefficients (and hence, a band-structure equation as given by the compatibility condition). But now we face another problem: Which one of Eqs. (23) and (25) is suitable to be introduced into Eq. (8)? In other words, which one correctly describes the Bloch function in Eq. (8), i.e., as an element of the Hilbert space $\mathcal{H}(\boldsymbol{\kappa})$? The sums in both Eqs. (23) and (25) have, as their result, the same Bloch function (we will later see an example) and even worse, there is yet a third candidate, namely the superposition (familiar in multiple-scattering theory[2])

$$f(\boldsymbol{\kappa},E,\boldsymbol{\rho})=\sum_{L}\Phi^{\text{cell}}_{L}(E,\boldsymbol{\rho})A_L(\boldsymbol{\kappa},E)\ , \tag{27}$$

where $\Phi^{\text{cell}}_{L}(E,\boldsymbol{\rho})$ denotes the regular solutions of the cell potential with boundary conditions Eq. (14). [These functions are given by Eq. (22a) with V^d replaced by $\mathcal{V}$. Long ago,[16] such a superposition was considered to correctly describe the Bloch function; recently,[2,3,5,6] it was considered as an approximation.]

Thus, irrespective of whether the periodic potential is of muffin-tin type or not, we now have three expressions, Eqs. (23), (25), and (27), for the Bloch function required in Eq. (8): First, Eqs. (23) and (25), when introduced in Eq. (8), surely produce a necessary condition for the coefficients A but we do not know whether it is also a sufficient one [e.g., since in Eq. (21) each individual term is not Bloch periodic but their sum has this property, Eq. (21) might produce, in conjunction with Eq. (15), other necessary conditions as well]. Second, provided Eq. (27) represents the Bloch function, it also generates, upon introduction into Eq. (8), a necessary condition which, again, might not be sufficient. Obviously, in the muffin-tin case, the consequences of using Eq. (27) will be the same as using Eq. (23); still, there exists a difference in using Eq. (23) or (25). For completeness, and also in order to illustrate the usefulness of Eq. (8), we now introduce each of Eqs. (23), (25), and (27) into Eq. (8) and discuss the corresponding results. In doing so, we will obtain various results derived previously[1–6] (by different means) and we will, in addition, derive a new result which, in the soluble case of the constant periodic potential, is shown analytically to generate the correct band structure. Finally, we will show how previous results (some claimed as exact[3,4]) can be obtained in the present approach as various approximations of the same (seemingly exact) result.

By introducing Eq. (23) into Eq. (8), we obtain

$$\sum_{L'}\mathscr{C}^{\text{circ}}_{LL'}(\boldsymbol{\kappa},E_n(\boldsymbol{\kappa}))A_{L'}(\boldsymbol{\kappa},E_n)=0 \tag{28}$$

where we introduced the matrices (in the L representation)

$$\begin{aligned}\underline{\mathscr{C}}^{\text{circ}}(\boldsymbol{\kappa},E)&=\underline{\Gamma}^{\text{circ}}(E)-\underline{\mathfrak{S}}^{\text{circ}}(\boldsymbol{\kappa},E)\ ,\\ \Gamma^{\text{circ}}_{LL'}(E)&=\delta_{LL'}-\frac{\pi\sqrt{E}}{2}\int_{\Omega}n^{*}_{L}(E,\boldsymbol{\rho})\mathcal{V}(\boldsymbol{\rho})\Phi^{\text{circ}}_{L'}(E,\boldsymbol{\rho})d\boldsymbol{\rho}\ ,\\ \mathfrak{S}^{\text{circ}}_{LL'}(\boldsymbol{\kappa},E)&=\frac{\pi\sqrt{E}}{2}\int_{\Omega}\mathfrak{n}^{*}_{L}(\boldsymbol{\kappa},E,\boldsymbol{\rho})\mathcal{V}(\boldsymbol{\rho})\Phi^{\text{circ}}_{L'}(E,\boldsymbol{\rho})d\boldsymbol{\rho}\ .\end{aligned} \tag{29}$$

(Notice the close similarity with the c and s coefficients of the usual variable-phase method;[12] hence, the notation.) Thus, the band-structure equation generated by the representation Eq. (23b) is given by

$$\det[\underline{\Gamma}^{\text{circ}}(E)-\underline{\mathfrak{S}}^{\text{circ}}(\boldsymbol{\kappa},E)]=0 \tag{30a}$$

and, by using Eqs. (9) and (11), we notice that the separation of the structure constant pertains to the factorization of the matrix $\underline{\mathfrak{S}}^{\text{circ}}(\boldsymbol{\kappa},E)$. Thus, since the matrix $\underline{\mathfrak{S}}^{\text{circ}}(\boldsymbol{\kappa},E)$ can be factorized only in the case of closed-packed lattices, Eq. (11), we have (only) in this case

$$\det[\underline{\Gamma}^{\text{circ}}(E)-\underline{N}(\boldsymbol{\kappa},E)\underline{\Sigma}^{\text{circ}}(E)]=0\ . \tag{30b}$$

Here we have introduced

$$\Sigma^{\text{circ}}_{LL'}(E)=\frac{\pi\sqrt{E}}{2}\int_{\Omega}j^{*}_{L}(E,\boldsymbol{\rho})\mathcal{V}(\boldsymbol{\rho})\Phi^{\text{circ}}_{L'}(E,\boldsymbol{\rho})d\boldsymbol{\rho}\ , \tag{31}$$

and $\underline{N}(\boldsymbol{\kappa},E)$ represents the usual structure constants.[1] In Eq. (30b), the lattice structure contribution (that is, the $\boldsymbol{\kappa}$ dependence) was separated from the potential contribution (akin to the KKR equation) but (in contradistinction to the KKR equation) the matrix $\underline{\Sigma}^{\text{circ}}(E)[\underline{\Gamma}^{\text{circ}}(E)]^{-1}$ does not represent the (principal value) t matrix of the unit cell. The band-structure equation given by Eq. (30b) was first derived in Ref. 3 and claimed to be exact; subsequently, its exactness was questioned on both computational[7] and analytical grounds.[4] In the present approach, Eq. (31) reflects a necessary condition, namely Eq. (28); but as already stated, its sufficiency is doubtful [because Eq. (23b) might generate, in conjunction with Eq. (15), other conditions for the A_L coefficients]. In Sec. IV it will be shown (by examining a soluble case) that Eq. (30b) cannot represent an exact result.

By considering that the Bloch function can be described as an on-shell superposition of the regular solutions corresponding to the cell potential, Eq. (27), we obtain

$$\sum_{L'} \mathcal{C}^{\text{cell}}_{LL'}(\boldsymbol{\kappa},E_n(\boldsymbol{\kappa}))\,A_{L'}(\boldsymbol{\kappa},E_n)=0 \ , \tag{32}$$

where we introduced the matrices

$$\begin{gathered}\underline{\mathcal{C}}^{\text{cell}}(\boldsymbol{\kappa},E)=\underline{\Gamma}^{\text{cell}}(E)-\underline{\mathfrak{S}}^{\text{cell}}(\boldsymbol{\kappa},E) \ , \\ \Gamma^{\text{cell}}_{LL'}(E)=\delta_{LL'}-\frac{\pi\sqrt{E}}{2}\int_{\Omega} n^{*}_{L}(E,\boldsymbol{\rho})\mathcal{V}(\boldsymbol{\rho})\Phi^{\text{cell}}_{L'}(E,\boldsymbol{\rho})d\boldsymbol{\rho} \ , \\ \mathfrak{S}^{\text{cell}}_{LL'}(\boldsymbol{\kappa},E)=\frac{\pi\sqrt{E}}{2}\int_{\Omega} \mathfrak{n}^{*}_{L}(\boldsymbol{\kappa},E,\boldsymbol{\rho})\mathcal{V}(\boldsymbol{\rho})\Phi^{\text{cell}}_{L'}(E,\boldsymbol{\rho})d\boldsymbol{\rho} \ .\end{gathered} \tag{33}$$

Hence, if one supposes that the Bloch function is given by Eq. (27), then the band-structure equation is given by

$$\det[\underline{\Gamma}^{\text{cell}}(E)-\underline{\mathfrak{S}}^{\text{cell}}(\boldsymbol{\kappa},E)]=0 \tag{34a}$$

which, in the case of closed-packed lattices, can be further simplified [again, from Eqs. (9) and (11)]

$$\det[\underline{\Gamma}^{\text{cell}}(E)-\underline{N}(\boldsymbol{\kappa},E)\underline{\Sigma}^{\text{cell}}(E)]=0 \ , \tag{34b}$$

where we introduced

$$\Sigma^{\text{cell}}_{LL'}(E)=\frac{\pi\sqrt{E}}{2}\int_{\Omega} j^{*}_{L}(E,\boldsymbol{\rho})\mathcal{V}(\boldsymbol{\rho})\Phi^{\text{cell}}_{L'}(E,\boldsymbol{\rho})d\boldsymbol{\rho} \ . \tag{35}$$

In this case, the structure is not only separated from the potential but the matrix $\underline{\Sigma}^{\text{cell}}(E)[\underline{\Gamma}^{\text{cell}}(E)]^{-1}$ represents the (principal value) t matrix of the unit cell, in complete analogy to the KKR equation. This result was first derived in Ref. 16 on the ground that the functions $\Phi^{\text{cell}}_{L}(E,\mathbf{r})$, being a complete set, can describe the Bloch function as an on-shell superposition. While this motivation is erroneous [because the functions $\Phi^{\text{cell}}_{L}(E,\mathbf{r})$ form a complete set in $L^2(R^3)$ whereas the Bloch functions belong to another Hilbert space], the above representation itself [and hence Eq. (34b)] might still be true. Nevertheless, as was shown by using various means,[2,3,5,6] Eq. (34b) does not represent an exact result [recently, however, as an exception, Ref. 4 claimed to derive Eq. (34b) as an exact result]. From our results, it follows that Eq. (34b) represents an approximate result since the Bloch function cannot be described as given by Eq. (27) for $\rho\in\Omega$ but $\rho\geq\mu$. Actually, from Eq. (5), by using Eq. (6), one derives Eq. (23b) which, from Eq. (22b), coincides with Eq. (27) only for $\rho\leq\mu$. The soluble case examined in Sec. IV will make this point more apparent.

Finally, if we consider the particular case of a muffin-tin potential, then Eq. (34b) coincides with Eq. (30b) and both of them further coincide with the well-known KKR equation.[1] Even in this case, however, the problem remains whether the periodicity condition, Eq. (15), imposes some supplementary conditions upon the A_L coefficients of the superposition Eq. (23). Unfortunately (in contrast to the full potential case, see Sec. IV), there is no soluble case of the muffin-tin type (except for the Kronnig-Penney δ-function model, which is trivial) for which one can test whether the above equations are exact (i.e., generate the same results as that given by the plane-wave diagonalization).

So far, we have seen that different representations of the Bloch function can generate, upon introduction in Eq. (8), different band-structure equations. Now, we examine the result produced by the on-shell Bloch periodic representation, Eqs. (25) and (26).

III. A NEW BAND-STRUCTURE EQUATION AND PERIODICITY CORRECTIONS

By introducing Eq. (25b) into Eq. (8), we obtain

$$\sum_{L'} \mathcal{C}^{d}_{LL'}(\boldsymbol{\kappa},E_n(\boldsymbol{\kappa}))\,A_{L'}(\boldsymbol{\kappa},E_n)=0 \ , \tag{36}$$

where we introduced the abbreviations

$$\begin{gathered}\underline{\mathcal{C}}^{d}(\boldsymbol{\kappa},E)=\underline{\Gamma}^{d}(\boldsymbol{\kappa},E)-\underline{\mathfrak{S}}^{d}(\boldsymbol{\kappa},E) \ , \\ \Gamma^{d}_{LL'}(\boldsymbol{\kappa},E)=\delta_{LL'}-\frac{\pi\sqrt{E}}{2}\int_{\Omega} n^{*}_{L}(E,\boldsymbol{\rho})\mathcal{V}(\boldsymbol{\rho})\tilde{\Phi}^{d}_{L'}(\boldsymbol{\kappa},E,\boldsymbol{\rho})d\boldsymbol{\rho} \ . \\ \mathfrak{S}^{d}_{LL'}(\boldsymbol{\kappa},E)=\frac{\pi\sqrt{E}}{2}\int_{\Omega} \mathfrak{n}^{*}_{L}(\boldsymbol{\kappa},E,\boldsymbol{\rho})\mathcal{V}(\boldsymbol{\rho})\tilde{\Phi}^{d}_{L'}(\boldsymbol{\kappa},E,\boldsymbol{\rho})d\boldsymbol{\rho} \ .\end{gathered} \tag{37}$$

Since it follows from Eq. (25) that Eq. (36) should be satisfied for any finite d, we have [by using Eq. (22b)]

$$\det[\underline{\Gamma}(\boldsymbol{\kappa},E)-\underline{\mathfrak{S}}(\boldsymbol{\kappa},E)] \equiv \lim_{d\to\infty}\det[\underline{\Gamma}^{d}(\boldsymbol{\kappa},E)-\underline{\mathfrak{S}}^{d}(\boldsymbol{\kappa},E)]=0 \tag{38a}$$

which, in the case of closed-packed lattices, becomes [from Eqs. (9) and (11)]

$$\det[\underline{\Gamma}(\boldsymbol{\kappa},E)-\underline{N}(\boldsymbol{\kappa},E)\underline{\Sigma}(\boldsymbol{\kappa},E)]=0 \ , \tag{38b}$$

where we introduced

$$\Sigma^{d}_{LL'}(\boldsymbol{\kappa},E)=\frac{\pi\sqrt{E}}{2}\int_{\Omega} j^{*}_{L}(E,\boldsymbol{\rho})\mathcal{V}(\boldsymbol{\rho})\tilde{\Phi}^{d}_{L'}(\boldsymbol{\kappa},E,\boldsymbol{\rho})d\boldsymbol{\rho} \ . \tag{39}$$

From the definition of the limit, it is clear that the equations

$$\det[\underline{\Gamma}^{d}(\boldsymbol{\kappa},E)-\underline{\mathfrak{S}}^{d}(\boldsymbol{\kappa},E)]=0 \ , \tag{40a}$$

$$\det[\underline{\Gamma}^{d}(\boldsymbol{\kappa},E)-\underline{N}(\boldsymbol{\kappa},E)\underline{\Sigma}^{d}(\boldsymbol{\kappa},E)]=0 \tag{40b}$$

offer a sequence of approximations to the band-structure equation, and in the limit $d\to\infty$ it yields the result as defined by Eqs. (38) and (39).

Equation (38) contains our main result; it represents a new band-structure equation which will be shown to produce, in contradistinction to the previous attempts,[1-6] the correct energy levels of the constant periodic potential (the empty lattice test). While this feature suggests that Eq. (38) represents, in fact, an exact result for a general periodic potential, it is, however, not a proof. Therefore, we consider, hereafter, Eq. (38) only as a necessary condition (by construction) and discuss its relation with previously derived results. Also, in discussing the soluble case of a constant periodic potential we will try to find out the factor that is responsible for the exactness of Eq. (38) in this particular case. [This offers a hint in searching for the exactness of Eq. (38) with a general periodic potential.]

In comparison with earlier results,[1-6] Eq. (38) exhibits a supplementary $\boldsymbol{\kappa}$ dependence, that is, a supplementary structure dependence. More precisely, the lattice structure enters Eq. (38) not only by means of the function $\mathrm{n}(\boldsymbol{\kappa},E,\boldsymbol{\rho})$ defined in Eq. (9b) but also by means of the Γ and Σ matrices. However, in view of computational results obtained in Ref. 7, the main structure dependence is contained in the function $\mathrm{n}(\boldsymbol{\kappa},E,\boldsymbol{\rho})$ and the $\boldsymbol{\kappa}$ dependence of the Γ and Σ matrices is expected to represent a correction. This correction (as a supplementary $\boldsymbol{\kappa}$ dependence) is introduced in Eq. (8) by the use of a representation, Eq. (25), which, in the limit $d=\infty$, identically satisfies the Bloch periodicity Eq. (15). In other words, by representing the Bloch function in Eq. (8) in terms of Eq. (25), the A_L coefficients then appear to be subject to Eq. (8) only. This is another hint for the exactness of Eq. (38), but again is not a proof [for even if Eq. (38) contains all the conditions upon the coefficients A_L, it may have solutions other than the band structure]. Thus, the essential way in which Eq. (38) differs from all the previous attempts[1-6] is represented by the above-mentioned supplementary $\boldsymbol{\kappa}$ dependence [which, however, seems to indicate that Eq. (38) is rather an exact result]. This supplementary $\boldsymbol{\kappa}$ dependence can be isolated by using Eq. (26e) and introducing the matrices

$$\begin{aligned}
&\underline{\Delta}^d(\boldsymbol{\kappa},E)=\underline{\gamma}^d(\boldsymbol{\kappa},E)-\underline{c}^d(\boldsymbol{\kappa},E)\ ,\\
&\gamma^d_{LL'}(\boldsymbol{\kappa},E)=(-)\frac{\pi\sqrt{E}}{2}\int_\Omega n^*_L(E,\boldsymbol{\rho})\mathcal{V}(\boldsymbol{\rho})\\
&\qquad\qquad\times\varphi^d_{L'}(\boldsymbol{\kappa},E,\boldsymbol{\rho})d\boldsymbol{\rho}\ ,\\
&c^d_{LL'}(\boldsymbol{\kappa},E)=\frac{\pi\sqrt{E}}{2}\int_\Omega \mathrm{n}^*_L(\boldsymbol{\kappa},E,\boldsymbol{\rho})\mathcal{V}(\boldsymbol{\rho})\varphi^d_{L'}(\boldsymbol{\kappa},E,\boldsymbol{\rho})d\boldsymbol{\rho}\ ,\\
&\sigma^d_{LL'}(\boldsymbol{\kappa},E)=\frac{\pi\sqrt{E}}{2}\int_\Omega j^*_L(E,\boldsymbol{\rho})\mathcal{V}(\boldsymbol{\rho})\varphi^d_{L'}(\boldsymbol{\kappa},E,\boldsymbol{\rho})d\boldsymbol{\rho}\ .
\end{aligned}\tag{41}$$

Thus, the matrix in Eq. (38) can be expressed as [compare with Eqs. (28) and (30a)]

$$\underline{\mathscr{C}}(\boldsymbol{\kappa},E)=\underline{\mathscr{C}}^{\mathrm{circ}}(\boldsymbol{\kappa},E)+\lim_{d\to\infty}\underline{\Delta}^d(\boldsymbol{\kappa},E)\tag{42}$$

or, by using Eq. (26c) and introducing an obvious notation [similar to Eqs. (33) and (34)], we obtain

$$\begin{aligned}
\underline{\mathscr{C}}(\boldsymbol{\kappa},E)&=\underline{\mathscr{C}}^{\mathrm{MT}}(\boldsymbol{\kappa},E)\\
&\quad-\lim_{d\to\infty}\frac{\pi\sqrt{E}}{2}\int_{\Omega\setminus S^{\mathrm{MT}}} n^*_L(\boldsymbol{\kappa},E,\boldsymbol{\rho})\mathcal{V}(\rho)\\
&\qquad\times\tilde{\Phi}^d_{L'}(\boldsymbol{\kappa},E,\boldsymbol{\rho})d\boldsymbol{\rho}\ ,
\end{aligned}\tag{43}$$

$$\underline{\mathscr{C}}^{\mathrm{MT}}(\boldsymbol{\kappa},E)=\underline{\Gamma}^{\mathrm{MT}}(E)-\underline{N}(\boldsymbol{\kappa},E)\underline{\Sigma}^{\mathrm{MT}}(E)$$

(which contains the muffin-tin case). However, it should be mentioned that in Eq. (26c) the A_L coefficients are constrainted by a matching condition on the surface of the inscribed sphere [whereas in Eq. (25) these coefficients are free of any of such imposition].

Therefore, Eq. (38) introduces a specific correction to the previous results[1-6] which correction does not appear to be connected with the "near-field corrections" as usually discussed in the literature.[2] [In our approach, these "near-field corrections" are connected with the factorization of the matrix $\underline{\mathfrak{G}}^d(\boldsymbol{\kappa},E)$ which, in turn, relies on Eqs. (9) and (11).] Since the corrections defined in Eq. (41) reflect the Bloch periodicity in conjunction with the multipole expansion,[11] we can call them "multipole expansion periodicity corrections" or simply "periodicity corrections." Their importance will be seen from the soluble case discussed in the next section: The correct band structure for a constant periodic potential cannot be obtained from either Eq. (30a) or Eq. (34a) but only from Eq. (38). [Both Eqs. (30a) and (34a) yield a systematic error which cannot be decreased by increasing the L space.[7]] Finally, from a computational point of view, the question remains how fast is the d convergence in Eq. (42); this, in fact, reverts to the question of the numerical opportunities offered by the representation Eq. (26c) versus representation Eq. (26d). Obviously, this can be decided only by doing the computation; however, since the first term in Eq. (42) already gives a decent accuracy,[7] we might expect that the "periodicity corrections," even for small d, i.e., of the order of the circumscribing sphere, might offer better computational opportunities than the plane-wave expansion in the interstitial region.

IV. A SOLUBLE CASE: CONSTANT PERIODIC POTENTIAL

So far, we have seen that various representations of the Bloch function lead, by means of Eq. (8), to various band-structure equations (some claimed as an exact result[3,4]); among them, only Eq. (38) considers the Bloch function as a superposition of Bloch periodic orbitals, i.e., as an element of the Hilbert space $\mathscr{H}(\boldsymbol{\kappa})$. However, one can argue that all the band-structure equations mentioned above reflect only a necessary condition, Eq. (8), and therefore, unless the contrary is proven, they are correct (or incorrect) on an equal footing. For this reason, it is particularly useful to consider a soluble example and we choose the case of a constant periodic potential. In this sense, the present section is the analytic counterpart of Ref. 7 which considers the same potential and very carefully investigates the numerical solutions of Eqs. (30b) and (34b) for the case of closed-packed lattices.

Consider the constant periodic potential $V\geq 0$; the solutions of the eigenvalue equation (5) are given by

$$\Psi(\boldsymbol{\kappa},E_{\mathbf{K}},\boldsymbol{\rho})=\frac{e^{i(\boldsymbol{\kappa}+\mathbf{K})\cdot\boldsymbol{\rho}}}{\sqrt{\omega}},\quad E_{\mathbf{K}}(\boldsymbol{\kappa})=(\boldsymbol{\kappa}+\mathbf{K})^2+V\tag{44a}$$

and the prolongation, defined by Eq. (15), is given by

$$\begin{aligned}
\Psi^d(\boldsymbol{\kappa},E_{\mathbf{K}},\mathbf{r})&=\frac{e^{i(\boldsymbol{\kappa}+\mathbf{K})\cdot\mathbf{r}}}{\sqrt{\omega}}\\
&=\sqrt{\varpi}\sum_L i^l j_L[(\boldsymbol{\kappa}+\mathbf{K})^2,\mathbf{r}]Y^*_L(\hat{\mathscr{H}}),\quad r\leq d\ ,
\end{aligned}\tag{44b}$$

where we used the decomposition of the plane wave into spherical waves, and $\mathscr{H}=\boldsymbol{\kappa}+\mathbf{K}$. The regular solutions of Eq. (22) inside the sphere $r\leq d$ are given by

$$\Phi_L^d(E,\mathbf{r})=\left[\frac{E}{E-V}\right]^{l/2} j_L(E-V,\mathbf{r}), \quad r\le d \tag{45a}$$

and we recall the Fourier transform

$$j_L(E,\mathbf{r})=\sum_{\mathbf{K}}\int d\boldsymbol{\kappa}\frac{e^{i(\boldsymbol{\kappa}+\mathbf{K})\cdot\mathbf{r}}}{(2\pi)^{3/2}}\frac{\delta(\sqrt{E}-[(\boldsymbol{\kappa}+\mathbf{K})^2]^{1/2})}{E} \times i^{-l}Y_L(\hat{\mathcal{K}}) . \tag{45b}$$

Then, the existence of a decomposition as given by Eq. (21) is made obvious. Also, from Eq. (45b), we notice that in the limit $d=\infty$ the regular solution of Eq. (22) becomes an on-shell superposition of the corresponding Bloch functions. More than that, by comparing Eq. (44b) with Eq. (45), we find

$$A_L(\boldsymbol{\kappa},E)=\sqrt{\tilde{\omega}}\left[\frac{E-V}{E}\right]^{l/2} i^l Y_L^*(\hat{\mathcal{K}}) , \quad E=E_K . \tag{46}$$

On the other hand, the coefficients $A_L(\boldsymbol{\kappa},E_{\mathbf{K}})$ are defined by Eq. (8) where the corresponding Bloch function was given in Eq. (44a). By using Eq. (10) we easily find that Eq. (8) yields the same result as given by Eq. (46).

Now, in view of the construction in Eq. (26a) and (26b), we recall the translational property

$$j_L(E,\mathbf{r}+\mathbf{r}')=\sum_{L'} j_{L'}(E,\mathbf{r})J_{L'L}(E,\mathbf{r}') , \tag{47}$$

where the matrix $J_{L'L}(E,\mathbf{r}')$, given, e.g., in Ref. 10, can be easily seen to satisfy the relation

$$\sum_L J_{L'L}(E,\mathbf{r})i^l Y_L^*(\hat{\mathbf{p}})=e^{i\sqrt{E}\hat{\mathbf{p}}\cdot\mathbf{r}}i^{l'}Y_{L'}^*(\hat{\mathbf{p}}) . \tag{48}$$

In conjunction with Eq. (46), Eqs. (47) and (48) prove the existence of the representation Eq. (25) for a constant periodic potential.

Finally, in view of the band-structure equation as defined by Eqs. (38) and (39), we calculate the function $\tilde{\Phi}_L(\boldsymbol{\kappa},E,\boldsymbol{\rho})$ defined by the limit $d=\infty$ of Eqs. (26a) and (26b). First, by using the expression[10] for the matrix $J_{L'L}(E,\mathbf{r})$, the decomposition of the plane wave into spherical waves and the definition of the δ function,

$$\delta(x)=\frac{1}{(2\pi)}\int e^{ipx}dp ,$$

we evaluate the sum

$$J_{L'L}(\boldsymbol{\kappa},E)=\sum_{\mathbf{R}} e^{-i\boldsymbol{\kappa}\cdot\mathbf{R}}J_{L'L}(E,\mathbf{R}) =\tilde{\omega}i^{l'-l}\sum_{\mathbf{K}} Y_{L'}^*(\hat{\mathcal{K}})\frac{\delta(\sqrt{E}-[(\boldsymbol{\kappa}+\mathbf{K})^2]^{1/2})}{E}Y_L(\hat{\mathcal{K}}) \tag{49}$$

and then, from Eqs. (24), (26a), (26b), (47), and (49), we obtain

$$\tilde{\Phi}_L(\boldsymbol{\kappa},E,\boldsymbol{\rho})=\sum_{\mathbf{K}}\frac{e^{i(\boldsymbol{\kappa}+\mathbf{K})\cdot\boldsymbol{\rho}}}{\sqrt{\omega}}\left[\lim_{N_\Omega\to\infty}\frac{\sqrt{\tilde{\omega}}}{N_\Omega}\frac{\delta(\sqrt{(E-V)}-[(\boldsymbol{\kappa}+\mathbf{K})^2]^{1/2})}{E-V}\left[\frac{E}{E-V}\right]^{l/2} i^{-l}Y_L(\hat{\mathcal{K}})\right] . \tag{50}$$

Thus, we notice that, in the limit $d=\infty$, the function $\tilde{\Phi}_L^d(\boldsymbol{\kappa},E,\boldsymbol{\rho})$ defined in Eq. (26a) becomes a superposition of the corresponding Bloch functions, and the coefficients are not numbers but rather distributions; clearly this originates in the existence of the Fourier transform, Eq. (45b). By now using Eqs. (50) and (10) in Eq. (38), we obtain

$$\mathcal{C}_{LL'}(\boldsymbol{\kappa},E)=\delta_{LL'}-\sum_{\mathbf{K}}\left[\frac{(\boldsymbol{\kappa}+\mathbf{K})^2}{E}\right]^{l/2} i^l Y_L^*(\hat{\mathcal{K}})\frac{V}{E-(\boldsymbol{\kappa}+\mathbf{K})^2} \times\left[\lim_{N_\Omega\to\infty}\frac{\sqrt{\tilde{\omega}}}{N_\Omega}\frac{\delta(\sqrt{(E-V)}-[(\boldsymbol{\kappa}+\mathbf{K})^2]^{1/2})}{E-V}\left[\frac{E}{E-V}\right]^{l'/2} i^{-l'}Y_{L'}(\hat{\mathcal{K}})\right] \tag{51}$$

where we recall the usual summation relations[17]

$$\sum_{\mathbf{R}} e^{-i\mathbf{k}\cdot\mathbf{R}}=\tilde{\omega}\sum_{\mathbf{K}}\delta(\mathbf{k}-\mathbf{K}) ,$$
$$\lim_{N_\Omega\to\infty}\frac{1}{N_\Omega}\sum_{\mathbf{R}} e^{-i(\boldsymbol{\kappa}-\boldsymbol{\kappa}')\cdot\mathbf{R}}=\begin{cases}1 & \text{if } \boldsymbol{\kappa}=\boldsymbol{\kappa}',\\ 0 & \text{otherwise} .\end{cases} \tag{52}$$

and decomposition of the three-dimensional δ function in spherical coordinates

$$\delta(\mathbf{k}-\mathbf{k}')=\frac{\delta(k-k')}{k^2}\delta(\hat{\mathbf{k}}-\hat{\mathbf{k}}') =\frac{\delta(k-k')}{k^2}\sum_L Y_L(\hat{\mathbf{k}})Y_L^*(\hat{\mathbf{k}}') . \tag{53}$$

From relations (52) and (53) we infer that the only nontrivial solutions of the (homogeneous) system

$$\sum_L \mathcal{C}_{LL'}(\boldsymbol{\kappa},E)A_{L'}=0 , \tag{54}$$

where $A_{L'}(\boldsymbol{\kappa},E)$ and E are unknown, are given (up to an arbitrary normalization for the A_L coefficients) by

$$A_L=\left[\frac{E-V}{E}\right]^{l/2} i^l Y_L^*(\hat{\mathcal{K}}) , \quad E=E_{\mathbf{K}}=V+(\boldsymbol{\kappa}+\mathbf{K})^2 \tag{55}$$

as expected, according to Eqs. (44) and (46). Thus, we have seen that Eq. (38) can be solved for the case of a constant periodic potential and that it yields the correct band structure and wave functions.

From this example we learn several things. First and foremost, this is the first time that a KKR-type equation gives the correct (exact) result for the empty lattice test. Apparently, this is due to the "multipole expansion periodicity corrections" defined in Eqs. (41) to (43); that is, to the use in Eq. (8) of the on-shell Bloch periodic superposition, Eq. (25) [and not Eqs. (23) or (27)] as well as to the properties of Eq. (50) which, in turn, rely on Eq. (45). Clearly, this suggests that a proof for the exactness of Eq. (38) in the general case of an arbitrary periodic potential V will consist mostly in finding the meaning of the regular solution of Eq. (22) in the limit $d=\infty$; actually, suppose that in this limit the function $\Phi_L^d(E,\mathbf{r})$ becomes an on-shell superposition of the Bloch function corresponding to the potential V,[18] then the periodic orbitals, Eq. (26), will be expressed in terms of the Bloch functions as in Eq. (50), and therefore, the proof will follow the same line as in Eqs. (50)–(55).

Also, we learn from Eq. (44b) that the representation of Bloch functions as a superposition of regular solutions of the cell potential, Eq. (27), cannot be true and hence Eq. (34) cannot represent an exact result.

Finally, by identifying in Eq. (51) the terms which define the corresponding matrix $\underline{\mathcal{C}}^{\mathrm{circ}}(\boldsymbol{\kappa},E)$, Eq. (29), we conclude that Eq. (30) cannot represent an exact result. However, the intriguing point remains that (at least in the case of constant periodic potential) both Eqs. (30b) and (34b) give the same result which is systematically shifted from the correct one.[7,3] The next section addresses this point.

V. THE GENERALIZED MUFFIN-TIN APPROXIMATION

So far, we have seen that there are the "multipole expansion periodicity corrections" which allow us to obtain the correct result in the soluble case treated above. As a way of enhancing the understanding of these corrections, we now examine the conditions under which they may be disregarded. Before proceeding, we notice that these corrections appear to be directly connected with the representation of the Bloch function as a superposition in the space $\mathcal{H}(\boldsymbol{\kappa})$, i.e., Eq. (25) and not Eq. (23) or (27); alternatively, the A_L coefficients in Eq. (25) appear to be constrained only by Eq. (8) whereas in Eq. (23) they might be also constrained by the system of equations obtained upon introduction of Eq. (21) into Eq. (15). Finally, the KKR equation is obtained by simply introducing Eq. (23) into Eq. (8) for a muffin-tin potential and disregarding other if any, supplementary constraints coming from the Bloch periodicity requirements (as mentioned above).

Consider the situation depicted in Fig. 2; the dashed area is denoted by Ω_ε and, in the limit $\varepsilon=0$, it coincides with the whole unit cell Ω. Now, assume that the potential $\mathcal{V}_\varepsilon$ is defined by

$$\mathcal{V}_\varepsilon(\boldsymbol{\rho})=\begin{cases}\mathcal{V}(\boldsymbol{\rho}) & \text{for } \boldsymbol{\rho}\in\Omega_\varepsilon,\\ 0 & \text{elsewhere}\,.\end{cases} \tag{56}$$

Thus, since it is the product $\mathcal{V}\Psi$ which is needed in Eq. (8), we are interested, for any $\varepsilon\neq 0$, in using Eqs. (23), (25), or (27) only for $\boldsymbol{\rho}\in\mathrm{Int}\Omega$, i.e., the vector $\boldsymbol{\rho}$ does not touch the boundary of the unit cell. Now, we recall that at any such point, both the functions $\Phi_L^{\mathrm{cell}}(E,\boldsymbol{\rho})$ and $\Phi_L^{\mathrm{circ}}(E,\boldsymbol{\rho})$ can be represented as a superposition of the planes waves $(e^{i(\boldsymbol{\kappa}+\mathbf{K})\cdot\boldsymbol{\rho}}/\sqrt{\omega})_{\mathbf{K}}$ but this is no longer true at the boundary.[19] It follows that, at any interior point of Ω, Eq. (23b) can be (approximately) considered as a superposition in the space $\mathcal{H}(\boldsymbol{\kappa})$ and the same is true for Eq. (27) [provided the sum in Eq. (27) is convergent]. In other words, as long as we do not reach the boundary of the unit cell, it is reasonable to represent the Bloch function in Eq. (8) as a superposition of the regular solution of either the cell potential $\mathcal{V}$ or the potential $\mathcal{V}^{\mathrm{circ}}$ (since such a superposition satisfies the Schrödinger equation with the cell potential as a differential equation only, i.e., without boundary conditions, the above two superpositions are here on an equal footing). Thus, the band equation is given by Eqs. (30a) or (34a) which, essentially, (partially) breaks the Bloch periodicity [only partially, because the Bloch boundary conditions, i.e., the $\boldsymbol{\kappa}$ dependence is still contained in the function $\mathrm{n}(\boldsymbol{\kappa},E,\boldsymbol{\rho})$].

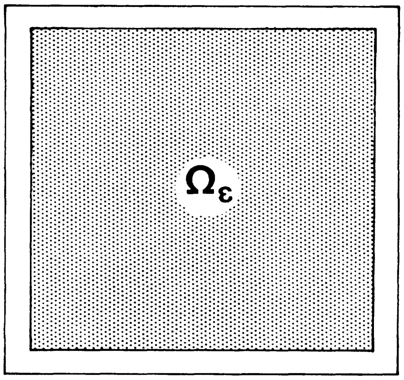

FIG. 2. Generalized muffin-tin approximation.

Now, consider $\varepsilon\to 0$; there are two possibilities

$$\lim_{\varepsilon\to 0}\mathcal{V}_\varepsilon(\boldsymbol{\rho})=\mathcal{V}(\boldsymbol{\rho})\quad\text{for any } \boldsymbol{\rho}\in\Omega \tag{57}$$

or

$$\lim_{\varepsilon\to 0}\mathcal{V}_\varepsilon(\boldsymbol{\rho})=\begin{cases}\mathcal{V}(\boldsymbol{\rho}) & \text{for } \boldsymbol{\rho}\in\mathrm{Int}\Omega,\\ 0 & \text{for } \boldsymbol{\rho} \text{ on the boundary of } \Omega\,.\end{cases} \tag{58}$$

The situation described by Eq. (57), clearly involves the Bloch function at the boundary of the unit cell, where Eqs. (23) and (27) can no longer be considered as superpositions in the space $\mathcal{H}(\boldsymbol{\kappa})$. Therefore, it is no longer reasonable to introduce these equations into Eq. (8) without considering the conditions obtained by introducing Eq. (23) into Eq. (15) which guarantees the Bloch periodicity.

In the second case (which is not physical because the potential has a discontinuity), we are interested only in the interior points of Ω and hence the band structure is still given (on an equal footing) by either Eq. (30a) or Eq. (34a). Thus, it appears that both these equations reasonably describe a potential which is zero at least in a small vicinity around the boundary of the unit cell. Since these band equations are obtained from Eq. (8) upon using only Eq. (23) or (27) (in complete analogy to the obtaining of the KKR equation mentioned in Sec. II), this situation can be called the "generalized muffin-tin approximation." This is the hidden approximation in both Refs. 3 and 4.

VI. SUMMARY AND CONCLUSIONS

We have considered the (integral) eigenvalue equation of the Bloch function and, with a view towards obtaining a KKR-type equation, we have examined various descriptions of the Bloch function as a multipole expansion. First, we have shown that the coefficients of the multipole series of the Bloch function around the origin assumes a particular form as a functional of the Bloch function and the cell potential, Eq. (8).

By introducing into this functional various representations of the Bloch function, Eqs. (23) and (27), and confining ourselves to the case of closed-packed lattices, we find the band-structure equation as previously derived[3,4] and claimed to be exact. The examination of a soluble case, however, shows (in agreement with a computational treatment[7]) that these band-structure equations cannot represent an exact result. Moreover, the consideration of the Bloch periodicity in conjunction with the existence of a multipole-expansion series shows that these band-structure equations express the same approximation, namely of using in Eq. (8) a representation of the Bloch function as a superposition which is not in the space of Bloch periodic functions (i.e., in which each individual term is not Bloch periodic). From the convergence properties of the Fourier series and from the need for the product $\mathcal{V}\Psi$ (not only Ψ) in Eq. (8), it follows that such an approximation is reasonable whenever the cell potential is zero in a small strip around the surface of the unit cell. Since the functional form of these approximate results is close to that of the KKR equation, we can call this situation the "generalized muffin-tin approximation."

However, since Eq. (8) reflects a property which takes place in the Hilbert space of Bloch periodic functions, it seems to be suitable to use in this equation a representation of the Bloch function as a superposition in the corresponding Hilbert space, Eq. (25). In doing so, we obtain a new band-structure equation which differs from the previous results,[1-6] by containing a very specific correction describing the Bloch periodicity within the multipole expansion and therefore called by us "multipole expansion periodicity corrections." In addition, this band-structure equation generates for the case of a constant periodic potential the correct eigenvalues, a feature which is not shared by any of the previous attempts. Thus, we have both theoretical and practical indications suggesting that Eq. (38) represents, in fact, an exact result (i.e., produces the same eigenvalues as the plane-wave diagonalization). This is borne out, in fact, by a T-operator analysis for a general periodic potential.[20]

ACKNOWLEDGMENTS

This work was supported by the National Science Foundation (DMR Grant No. 85-18607). Useful discussions with H.J.F. Jansen, M. Hwang, and R. Podloucky are gratefully acknowledged.

---

[1] J. Korringa, Physica, 6-7, 392 (1974); W. Kohn and N. Rostoker, Phys. Rev. **94**, 1111 (1954).

[2] J. S. Faulkner, Phys. Rev. B **19**, 6186 (1979), and references therein.

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

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

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

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

[7] J. S. Faulkner, [Phys. Rev. B **32**, 1339 (1985); **34**, 5931 (1986)], presents a pertinent account on the present "state of the art" in the separability between structure and potential and also gives a list of relevant references in the field. Particularly in the latest paper, he shows beyond any doubt (by performing clearly convergent computer calculations for cubic symmetry and constant potential) that the "near-field corrections," although small, are different from zero. Obviously, these corrections are expected to increase in the case of deformed unit cells.

[8] A preliminary communication was presented previously. See E. Badralexe and A. J. Freeman, Bull. Am. Phys. Soc. **31**, 255 (1986).

[9] Hereafter, we discuss only the case of positive energy, $E \geq 0$. For negative energy, $E < 0$, we should replace the kernel of the (Bloch periodic) Green function in Eq. (5), according to $\cos(\sqrt{E}r) \rightarrow e^{-\sqrt{-E}r}$. This results everywhere in changing $\sqrt{E} \rightarrow i\sqrt{-E}$ and $n_L \rightarrow j_L + in_L$.

[10] M. Donos and L. C. Maximan, J. Math. Phys. **6**, 766 (1964).

[11] The philosophy behind the introduction of the function $\Psi^d(\boldsymbol{\kappa}, E_n, \mathbf{r})$ can be summarized as follows. Consider a function $f^\Omega(\boldsymbol{\rho})$ defined on a nonspherical domain Ω. This function does not have a multipole expansion for we can calculate the integrals $f_L^\Omega(\rho) = \int_{4\pi} Y_L^*(\hat{\boldsymbol{\rho}}) f^\Omega(\boldsymbol{\rho}) d\hat{\boldsymbol{\rho}}$ only for those spheres which are included in Ω. However, we can build up various prolongations $f^S(\mathbf{r})$, defined in the circumscribing sphere S of Ω, and having the property $f^\Omega(\boldsymbol{\rho}) = f^S(\mathbf{r})\,|_{\mathbf{r}=\boldsymbol{\rho}\in\Omega}$. Every prolongation $f^S(\mathbf{r})$ has a multipole expansion and we also have $f^\Omega(\boldsymbol{\rho}) = \sum_L Y_L(\hat{\mathbf{r}}) f_L^S(r)\,|_{\mathbf{r}=\boldsymbol{\rho}\in\Omega}$. However, this is not a multipole expansion of $f^\Omega(\boldsymbol{\rho})$, for, by the way, it is nonunique. In the text, we choose a Bloch periodic prolongation because its equation can be derived simply from Eq. (5).

[12] Obviously, these functions are closely related to the usual Jost functions from ordinary scattering theory for the potential V^d. They can be computed with the variable phase method, as described in F. Calogero, *Variable Phase Approach to Potential Scattering* (Academic, New York, 1967), or, in a more fancy version, along the lines of C. Dullemond *et al.*, Comput. Phys. Commun. **27**, 377 (1982) or V. Rokhlin, J. Comput. Phys. **60**, 187 (1985).

[13] Such a representation is not new; it was previously addressed

in Refs. 2 and 3 but only for d as the radius of the circumscribing sphere and without noticing Eqs. (7) and (8) which, in the present paper, play the fundamental role.

[14] By construction, the limit $d=\infty$ in Eq. (26) should exist, though maybe in a distribution sense. More insight upon this point will be obtained in the next section, by means of a soluble case.

[15] J. C. Slater, Phys. Rev. **92**, 603 (1953); F. S. Ham and B. Segall, *ibid.* **124**, 1786 (1961).

[16] A. R. Williams and J. W. Morgan, J. Phys. C **7**, 37 (1974).

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

[18] It is well known [e.g., I. M. Gel'fand, Dokl. Akad. Nauk SSSR **73**, 1117 (1950)] that if $f(\mathbf{r})$ is square integrable, then we have $f(\mathbf{r})=\sum_n \int d\boldsymbol{\kappa}\, \Psi(\boldsymbol{\kappa},E_n,\mathbf{r})\hat{\mathbf{f}}_n$, where $\Psi(\boldsymbol{\kappa},E_n,\mathbf{r})$ are the Bloch functions of an arbitrary periodic potential and the coefficients are given by $\hat{\mathbf{f}}_n=\int \Psi^*(\boldsymbol{\kappa},E_n,\mathbf{r})f(\mathbf{r})d\mathbf{r}$. In our case, however, we need a stronger property [along the line of Eq. (45b)] which, essentially, gives the connection between the Hamiltonian $(-\Delta+V)$ in the space $L^2(R^3)$ and the Hamiltonian $(-\Delta+V)$ with Bloch periodic boundary conditions.

[19] Suppose the function $f(x)$, continuous in $[0,2\pi]$ and the corresponding Fourier coefficients $\hat{\mathbf{f}}_n=(1/2\pi)\int_0^{2\pi}e^{-inx}f(x)dx$. Then, the Fourier series $\sum_n e^{inx}\hat{\mathbf{f}}_n$ converges to $f(x)$ if $x\in(0,2\pi)$ and to $\frac{1}{2}[f(0)+f(2\pi)]$ at the end points. It follows that both the functions $\Phi_L^{\mathrm{circ}}(E,\boldsymbol{\rho})$ and $\Phi_L^{\mathrm{cell}}(E,\boldsymbol{\rho})$ can be represented at any interior point of Ω as a superposition of the plane wave $e^{i(\boldsymbol{\kappa}+\mathbf{K})\cdot\rho}$ but this superposition however, converges on the boundary towards $\frac{1}{2}[\Phi_L(E,\boldsymbol{\rho})+e^{-\boldsymbol{\kappa}\cdot\mathbf{R}}\Phi_L(E,\boldsymbol{\rho}+\mathbf{R})]$.

[20] E. Badralexe and A. J. Freeman, following paper, Phys. Rev. B **36**, 1389 (1987).