Eigenvalue equation for a general periodic potential and its multipole expansion solution

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It is shown that the Bloch function, as an element of the Hilbert space spanned by Bloch-periodic planes waves, can be also represented as an on-shell superposition of Bloch-periodic orbitals which, however, exist in a distribution sense. By using this result and the multipole expansion of the Bloch function at the origin, it is further shown that the integral eigenvalue equation of the Bloch function for a general periodic potential is equivalent (both necessary and sufficient) to an algebraic system of homogeneous linear equations for the coefficients of the multipole expansion of the Bloch function at the origin, akin to the much simpler case of a finite-range potential. In contrast to the Korringa-Kohn-Rostoker (KKR) equation, the contribution of the cell potential (whether of the muffin-tin or general form) introduces a supplementary structure dependence. However, the separation between structure and potential, typical for the KKR equation, can be restored by introducing various approximations.

I. INTRODUCTION

Although the formal theory of a periodic Hamiltonian has been well developed,[1,2] the existence of a computationally convenient procedure for the case of a general (non-Muffin-tin) potential still remains an open problem. A major accomplishment was achieved very early by Korringa,[3] and by Kohn and Rostoker[4] (KKR), with the introduction of the muffin-tin (MT) approximation.[5] In the spherical coordinates description (i.e., in the L representation), it is universally accepted that the MT potential allows the structure to be separated from the potential, and the energy bands are given as solutions of the KKR equation. Since then considerable attention has been focused on finding out in what sense, if any, the ordinary KKR equation can be generalized for a general (i.e., non-MT) periodic potential. That is, how can the general periodic potential be described in the L representation? Specifically, the question is to determine the extent to which the separation between structure and potential, so typical for the muffin-tin approximation, survives in the case of an arbitrary periodic potential. The continuing interest in this problem is motivated by the fact that such a separation is not only academically intriguing, but very useful in computational studies of ordered materials—particularly surfaces and interfaces—and almost a mandatory condition for impure or disordered materials, as in the KKR-CPA (coherent-potential approximation) method.

Until now, these investigations have been carried out mainly in the framework of multiple scattering theory and/or by use of the variational principle. The results obtained by various authors[6–15]—to cite only a few references—are seemingly in conflict.[13] More precisely, with a few exceptions,[9,10] all authors agree that the potential-structure separation is lost in the case of a (general) non-MT periodic potential, and therefore one has to consider the so-called "near-field corrections." Essentially, these corrections come from the mismatch between the nonsphericity of the unit cell and the L representation (spherical coordinate description) and their expression appears to be different from author to author (e.g., Refs. 7 and 8). Nevertheless, there is no soluble case in which one can study the role of these corrections analytically. As a result of some uncertainty in their expression, no attempts to compute these corrections have been reported.

For the close-packed lattices and a constant periodic potential, however, disregarding these corrections leads to results which seem to be reasonably good,[13] at least for present needs. Thus, for most of the authors, the "near-field corrections," although different from zero, are usually neglected and except for an upper bound (determined by neglecting them and comparing the result so obtained with the exact one in a soluble case[13]) no practical evaluation was done nor was any soluble case studied. Both Refs. 9 and 10 conclude, however, that in the case of close-packed lattices, the structure gets separated from the potential as an *exact* result, but they fail to agree on the analytic expression for the governing band-structure equation. Thus, Ref. 10 concludes that the band-structure equation derived previously[6] and known[7–9] to be approximate, is in fact an exact result, whereas Ref. 9 proposes a modification. As demonstrated in Ref. 13, by performing a highly accurate computation, both formulations 9 and 10 yield essentially the same accuracy as the usual approximate methods when computed in the case of a (non-MT) constant periodic potential. Unfortunately, numerical tests are the only ones available, since the equations given previously[9,10] are not known to admit relevant (full potential) soluble cases. (At least so far, these equations can be solved analytically only in the case of δ-function potentials, when they become identical and the result obtained coincides with that of the Kronnig-Penney model.) As discussed by us recently,[16] the results presented (as exact ones) in both Refs. 9 and 10 correspond in fact to an approximation which, essentially, breaks the Bloch periodi-

city of the Bloch function; since this approximation is more reasonable when the cell potential is zero in a vicinity of the boundary of the unit cell, it was called the "generalized muffin-tin approximation."

An interesting line of investigation has been developed recently which contrasts with the multiple scattering theory.[11] By the use of a variational principle, an R-matrix formalism is established for an (arbitrary shape) unit cell; after introducing an approximate trial function (which violates Bloch periodicity) and expanding in atomic cell orbitals (in analogy to the linear muffin-tin orbital method) the resulting approximate band-structure equation can be put in a form which essentially coincides with that presented (but claimed to be an exact result) in Refs. 6 and 10.

Also recently, a new and efficient computational procedure for the case of finite clusters was developed.[14] By expanding the scattering states around each center and by absorbing the contribution of the interstitial potential in a (slightly modified) T matrix, a multiple-scattering formalism was established which generalizes the muffin-tin case along lines previously mentioned.[15]

In a previous paper,[16] we discussed the problem of an energy band equation for a general, i.e., non-MT, periodic potential with a different approach from those known so far, i.e., multiple scattering and/or variational principle.[3-15] From the (integral) eigenvalue equation of the Bloch function, we derived, by means of a proper multipole expansion analysis, a new band-structure equation which differs from previous results[3-15] by containing a very specific term describing the Bloch periodicity within the multipole expansion (and therefore, called by us "multipole expansion periodicity corrections"). Although this new band-structure equation was shown analytically to yield the correct eigenvalues in the soluble case of a constant periodic potential (a result not achieved by any of the previous attempts[3-15]) it is not obvious that this is also the case for a general periodic potential. (The reason is simply that this new equation when applied to the general case might have roots other than those given by the plane-wave diagonalization.)

It is the purpose of this paper to show that the new band-structure equation introduced previously[16] yields the same eigenvalues as those obtained from the plane-wave diagonalization for *any* periodic potential and therefore represents an *exact* result. More generally, we show here that the eigenvalue equation of the Bloch function (in the Hilbert space of Bloch periodic functions) is equivalent (both necessary *and* sufficient) to a system of homogeneous linear equations for the coefficients of the multipole expansion of the Bloch function at the origin. The general philosophy consists in showing that the Bloch function (as a solution of a differential equation *plus* Bloch boundary condition) can also be described as a superposition of the regular solutions of the same differential equation which can be easily found with the variable-phase method.[17] The coefficients of this superposition are determined from the boundary conditions (which are contained in the eigenvalue equation) as satisfying a homogeneous linear system of equations. Hence the compatibility condition gives an equation for the energy, whose solutions are shown to be the same as those of the plane-wave diagonalization. As a matter of fact, this procedure is a particular reflection of a more general observation: the solution of a boundary problem (i.e., differential equation *plus* certain boundary conditions) can be expressed as a superposition of (arbitrary) independent solutions (in a Wronskian sense) of the differential equation and the coefficients are matched from the boundary conditions. This allows us to explicitly construct elements of a certain Hilbert space (in particular, the Hilbert space of the Bloch-periodic functions) by simply imposing certain boundary conditions (in particular, Bloch boundary conditions) upon the solution of a differential equation.

The paper is organized as follows: In Sec. II, we briefly present the main idea of the variable-phase method and, as a way of enhancing the understanding of the above procedure (and also for later reference), illustrate it in a simple case (a finite-range potential). In Sec. III we recall the (Bloch periodic) prolongation of the Bloch function in an arbitrary large sphere[16] and, in view of later developments, discuss in great detail the multipole expansion description of this prolongation. Subsequently, in Sec. IV, by using the Fourier transform of the regular solution for a potential which is periodic inside an arbitrary large sphere and zero outside, the multipole expansion is converted into an on-shell superposition of Bloch-periodic orbitals which exist in a distribution sense. (That is not too troublesome because we are interested in calculating integrals and not their point by point values.) In other words, we find a base in the Hilbert space of Bloch-periodic functions by which an arbitrary Bloch function can be represented as an on-shell superposition of Bloch-periodic orbitals. By using the results established in the previous sections, it is shown in Sec. V that the integral eigenvalue equation of the Bloch function can be transformed into a homogeneous algebraic system in terms of the regular solution of the differential equation, similar to the much simpler case of a finite-range potential presented in Sec. II. Finally, Sec. VI presents a summary and conclusions.

II. VARIABLE-PHASE METHOD, BOUND STATES, AND SCATTERING STATES FOR A FINITE-RANGE POTENTIAL

The variable-phase method converts the Schrödinger equation into a linear system of first-order differential equations (or into a linear system of Volterra-type integral equations) which can be solved more easily than the initial problem. We recall briefly here the basic idea of this method,[17] and transform the eigenvalue (homogeneous) integral equation of the bound states into a (homogeneous) algebraic system in terms of the regular solutions; similarly, the (inhomogeneous) integral equation of the scattering states is transformed into an (inhomogeneous) algebraic system in terms of the same regular solutions.

Consider the (partial derivative) equation

$$(\Delta+z^2)\Phi^d(z,\mathbf{r})=V^d(\mathbf{r})\Phi^d(z,\mathbf{r}) , \tag{1}$$

where z is an arbitrary complex number and assume that the potential $V^d(\mathbf{r})$ has a finite range denoted hereafter by d; provided that the potential is regular enough,[18] the following treatment does not depend on the (explicit) form of the potential which, in particular, can be chosen to be that of Eq. (29) below. Note that in this section, V^d denotes a potential which is regular enough[18] and otherwise arbitrarily chosen; in the next sections V^d will denote a particular potential as defined by Eq. (29) below.

Since Eq. (1) is defined over a spherical domain [in contrast with Eq. (31) below], we can separate the Laplacian in spherical coordinates and make use of the orthonormality of the spherical functions. Then any solution $\Phi^{d,\eta}(z,\mathbf{r})$ of Eq. (1), as given by a multipole expansion

$$\Phi^{d,\eta}(z,\mathbf{r})=\sum_L Y_L(\hat{\mathbf{r}})\phi_L^{d,\eta}(z,r), \quad \mathbf{r}=r\hat{\mathbf{r}} \tag{2}$$

is defined, up to (arbitrary) boundary conditions, by a coupled channel equation

$$\left[\frac{d}{dr}\left[r^2\frac{d}{dr}\right]+z^2r^2-l(l+1)\right]\phi_L^{d,\eta}(z,r) = \sum_{L'} V_{LL'}^d(r)\phi_{L'}^{d,\eta}(z,r)r^2 . \tag{3}$$

Here we introduced the matrix elements

$$V_{LL'}^d(r)=\int_{4\pi} Y_L^*(\hat{\mathbf{r}})V^d(\mathbf{r})Y_{L'}(\hat{\mathbf{r}})d\hat{\mathbf{r}} \tag{4}$$

and the index η in order to completely specify the function $\Phi^{d,\eta}(z,\mathbf{r})$ (later on, η will describe various boundary conditions). If the potential $V^d(\mathbf{r})$ is zero, then two independent solutions of Eq. (3) are given by the Bessel function, $j_l(zr)$, and Neumann function, $n_l(zr)$. Thus, in the spirit of the method of variation of the constants, we try to find the multipole components $\phi_L^{d,\eta}(z,r)$, in the form

$$\phi_L^{d,\eta}(z,r)=j_l(zr)C_L^{d,\eta}(z,r)+n_l(zr)S_L^{d,\eta}(z,r) , \tag{5}$$

where $C_L^{d,\eta}(z,r)$ and $S_L^{d,\eta}(z,r)$ are functions required to satisfy the relation

$$j_l(zr)\frac{d}{dr}C_L^{d,\eta}(z,r)+n_l(z,r)\frac{d}{dr}S_L^{d,\eta}(z,r)=0 \tag{6}$$

so as to provide continuity of radial derivative of the function $\Phi^{d,\eta}(z,\mathbf{r})$ across any spherical surface. A second equation for the derivatives of the coefficients $C_L^{d,\eta}(z,r)$ and $S_L^{d,\eta}(z,r)$ can be obtained by introducing Eq. (5) into Eq. (3) and using the Wronskian of the Bessel and Neumann functions; this finally results in the equations

$$\begin{aligned}\frac{d}{dr}C_L^{d,\eta}(z,r)&=-\frac{\pi z}{2}n_l(zr)\sum_{L'}V_{LL'}^d(r)\phi_{L'}^{d,\eta}(z,r)r^2 ,\\ \frac{d}{dr}S_L^{d,\eta}(z,r)&=\frac{\pi z}{2}j_l(zr)\sum_{L'}V_{LL'}^d(r)\phi_{L'}^{d,\eta}(z,r)r^2 ,\end{aligned} \tag{7}$$

where the function $\phi_L^{d,\eta}(z,r)$ is given by Eq. (5) and the potential $V^d(\mathbf{r})$ was supposed to be regular enough.[18] Alternatively, Eqs. (7) can be given in a Volterra-type integral version

$$\begin{aligned}C_L^{d,\eta}(z,r)&=C_L^{d,\eta}(z,r_0)-\frac{\pi z}{2}\int_{r_0}^r n_l(zr')\sum_{L'}V_{LL'}(r')\phi_{L'}^{d,\eta}(z,r')r'^2dr' ,\\ S_L^{d,\eta}(z,r)&=S_L^{d,\eta}(z,r_0)+\frac{\pi z}{2}\int_{r_0}^r j_l(zr')\sum_{L'}V_{LL'}(r')\phi_{L'}^{d,\eta}(z,r')r'^2dr' ,\end{aligned} \tag{8}$$

where the (arbitrary) initial conditions $C_L^{d,\eta}(z,r_0)$ and $S_L^{d,\eta}(z,r_0)$, at the (arbitrary) point $r=r_0$, are connected to the boundary conditions for Eq. (1). This connection becomes more apparent if we introduce Eq. (8) into Eq. (5) and rewrite Eq. (3) in the form

$$\phi_L^{d,\eta}(z,r)=\phi_{0_L}^{d,\eta}(z,r)+\frac{\pi z}{2}\int_{r_0}^r W_l(z,r,r')\sum_{L'}V_{LL'}(r')\phi_{L'}^{d,\eta}(z,r')r'^2dr' , \tag{9}$$

where we introduced the function

$$\phi_{0_L}^{d,\eta}(z,r)=j_l(zr)C_L^{d,\eta}(z,r_0)+n_l(zr)S_L^{d,\eta}(z,r_0) \tag{10}$$

and $W_l(z,r,r')$, which is defined by

$$W_l(z,r,r')=n_l(zr)j_l(zr')-j_l(zr)n_l(zr') , \tag{11}$$

is closely related to the Wronskian of Bessel and Neumann functions. Thus if the boundary condition for Eq. (1) can be described by means of a multipole expansion, then finding the solution of Eq. (1) is reduced to the integration of a linear system, Eq. (7) or (8) or (9). In particular, we are interested in the regular solution

$$\Phi_L^d(z,\mathbf{r})=\sum_{L'}Y_{L'}(\hat{\mathbf{r}})\phi_{L'L}^d(z,r) , \tag{12a}$$

$$\Phi_L^d(z,\mathbf{r})\to j_L(z,\mathbf{r}) \text{ as } r\to 0 , \tag{12b}$$

whose multipole components are given [from Eq. (8)] by

$$\begin{aligned}\phi_{L'L}^d(z,r)&=j_{l'}(zr)C_{L'L}^d(z,r)+n_{l'}(zr)S_{L'L}^d(z,r)\\ &=j_{l'}(zr)\delta_{LL'}\\ &\quad+\frac{\pi z}{2}\int_0^r W_{l'}(z,r,r')\\ &\qquad\times\sum_{L''}V_{L'L''}^d(r')\phi_{L''L}^d(z,r')r'^2dr' .\end{aligned} \tag{12c}$$

Here $j_L(z,\mathbf{r})$ stands, as usual, for the Bessel function

multiplied with the spherical function and similarly for $n_L(z,\mathbf{r})$. We are also interested in the irregular solutions

$$\Phi_L^{d,\lambda}(z,\mathbf{r})=\sum_{L'} Y_{L'}(\hat{\mathbf{r}})\phi_{L'L}^{d,\lambda}(z,r)\ , \tag{13a}$$

$$\Phi_L^{d,\lambda}(z,\mathbf{r})\rightarrow\lambda_L(z,\mathbf{r})\ \text{ as } r\rightarrow d\ , \tag{13b}$$

$$\begin{aligned}\phi_{L'L}^{d,\lambda}(z,r)&=j_{l'}(zr)C_{L'L}^{d,\lambda}(z,r)+n_{l'}(zr)S_{L'L}^{d,\lambda}(z,r)\\&=\lambda_{l'}(zr)\delta_{LL'}\\&\quad-\frac{\pi z}{2}\int_r^d W_{l'}(z,r,r')\\&\quad\times\sum_{L''}V_{L'L''}^d(r')\phi_{L''L}^{d,\lambda}(z,r')r'^2dr'\ ,\end{aligned} \tag{13c}$$

where λ stands for either a Bessel or Neumann function. Clearly, the irregular solutions, Eq. (13), are closely connected to the usual Jost functions; also, any superposition of regular solutions again represents a regular solution (but with other boundary conditions) whereas a superposition of irregular solutions can be a regular solution as well.

Thus we have seen that the boundary problem for a partial derivative equation, Eq. (1), can be converted into a first-order differential system or, alternatively, into a Volterra-type integral equation. The gain here is not only computational (which, however, is considerable) but also theoretical: Providing the solutions of Eq. (13) are known, by imposing proper boundary conditions upon a superposition of these solutions we then can explicitly construct physical states. These are elements of a certain Hilbert space which are usually found (by diagonalization in a certain base) in the form of an off-shell superposition. Hence, we have a method for explicitly finding the physical states: From their integral equation we determine boundary conditions of the type Eq. (10) and proceed by using Eq. (8), which results finally in expressing these physical states as on-shell superpositions.

As an example, consider the bound states $\Psi^d(E_n,\mathbf{r})$ with energy E_n as defined by the eigenvalue equation[19]

$$\Psi^d(E,\mathbf{r})=\frac{-1}{4\pi}\int\frac{\cos(E^{1/2}|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|}V^d(\mathbf{r}')\Psi^d(E,\mathbf{r}')d\mathbf{r}' \tag{14}$$

in the space of square integrable functions [usually denoted by $L^2(\mathbb{R}^3)$]. An immediate procedure to solve this equation would be to expand the eigenfunction

$$\Psi^d(E_n,\mathbf{r})=\sum_m\alpha_m(E_n)\xi_m(\mathbf{r}) \tag{15}$$

in a base which spans the space $L^2(\mathbb{R}^3)$ and, upon introduction into Eq. (44) or Eq. (1), to obtain a homogeneous algebraic system for the coefficients $\alpha_m(E_n)$ or an algebraic eigenvalue problem, respectively, which has to be solved by computer. In the superposition given by Eq. (15), each individual term expresses the boundary conditions [i.e., $\xi_m(\mathbf{r})$ belongs to $L^2(\mathbb{R}^3)$] and therefore, the coefficients are determined by the requirement that this superposition satisfies the Schrödinger equation only as a differential equation. Therefore, the solution given by Eq. (15) describes exactly the boundary conditions and (only) computationally satisfies the differential equation. It is also possible to realize the opposite situation, namely to exactly satisfy the differential equation and computationally the boundary conditions. This can be done by representing the solution of Eq. (14) as an on-shell superposition of the regular solutions, Eq. (12), and finding, from Eq. (14), the equation satisfied by the coefficients. Finally, this equation has to be solved by using the computer. Such a procedure is made possible by the multipole decomposition

$$\frac{-1}{4\pi}\frac{\cos E^{1/2}(|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|}=\frac{\pi E^{1/2}}{2}\sum_L j_L(E^{1/2},\mathbf{r}_<)n_L^*(E^{1/2},\mathbf{r}_>) \tag{16}$$

in conjunction with Eq. (8) or (9). Actually, from Eqs. (14) and (16), by using the behavior of the Bessel and Neumann functions at the origin, we find that the eigenfunction, i.e., solution of Eq. (14), satisfies the boundary condition

$$\Psi^d(E_n,\mathbf{r})\rightarrow\sum_L j_L(E_n^{1/2},\mathbf{r})A_L(E_n)\ \text{ as } \mathbf{r}\rightarrow\mathbf{0}\ , \tag{17}$$

where the

$$A_L(E_n)=\frac{\pi E_n^{1/2}}{2}\int n_L^*(E_n^{1/2},\mathbf{r})V^d(\mathbf{r})\Psi^d(E_n,\mathbf{r})d\mathbf{r} \tag{18}$$

are functionals of Ψ^d. Then, from the uniqueness of the eigenfunction and by using Eq. (12), it follows that the bound state $\Psi(E_n,r)$ can be represented as an on-shell superposition

$$\Psi^d(E_n,\mathbf{r})=\sum_L\Phi_L^d(E_n^{1/2},\mathbf{r})A_L(E_n) \tag{19}$$

which, when introduced into Eq. (18), results in a homogeneous linear system

$$\sum_L C_{L'L}^d(E_n^{1/2},d)A_L(E_n)=0\ , \tag{20}$$

where the matrix $\mathbf{C}^d(E^{1/2},r)$ was defined in Eq. (8), Clearly then, the eigenvalues E_n of the integral homogeneous equation (14) and the corresponding coefficients $A_L(E_n)$ of the expansion Eq. (19) are given by the solution of the following algebraic homogeneous linear system of equations (which is not an eigenvalue problem)

$$\sum_L C_{L'L}^d(E^{1/2},d)A_L=0\ , \tag{21}$$

where both E and the A_L are unknown; obviously the compatibility condition

$$\det\mathbf{C}^d(E^{1/2},d)=0 \tag{22a}$$

gives the E_n and hence, for each E_n we obtain a set of $A_L(E_n)$. Alternatively, the (positive) eigenvalues are given by the roots of

$$\det[\mathbf{C}^d(E^{1/2},d)\pm i\mathbf{S}^d(E^{1/2},d)]=0\ , \tag{22b}$$

which upon changing $E^{1/2}\rightarrow i(-E)^{1/2}$ gives the negative eigenvalues as well.[19] [The matrices $\mathbf{C}^d(E^{1/2},d)$ and $\mathbf{S}^d(E^{1/2},d)$ generalize the cosine and sine of the phase shifts of the scattering theory for a spherically symmetric potential and gives account only of that part of the potential V^d which is contained in the sphere with radius r—hence the abbreviation C and S and the name of the method.] Thus we have seen that the eigenvalue equation defined by Eq. (14) is equivalent to the system of Eqs. (19) and (21).

As another example (also for later use), the scattering states $\Psi_L^{d\pm}(E,\mathbf{r})$ defined by

$$\Psi_L^{d\pm}(E,\mathbf{r})=j_L(E^{1/2},\mathbf{r})+\frac{-1}{4\pi}\int\frac{e^{\pm iE^{1/2}|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|}\times V^d(\mathbf{r}')\Psi_L^{d\pm}(E,\mathbf{r}')d\mathbf{r}' \tag{23}$$

in the generalized $L^2(\mathbb{R}^3)$ space (i.e., including the functions normalized to a δ function) are found to be given by

$$\Psi_L^{d\pm}(E,\mathbf{r})=\sum_{L'}\Phi_{L'}^d(E^{1/2},\mathbf{r})[C^d(E^{1/2},d)\pm iS^d(E^{1/2},d)]^{-1}_{LL'} \tag{24}$$

which clearly exist at any energy which is not a bound state. Finally, at a bound-state energy, the function $\Phi_L^d(E_n^{1/2},\mathbf{r})$ is square integrable whereas at a scattering energy, $E\neq E_n$, we have the normalization (easily obtained by transforming the volume integral into surface ones and using the asymptotic behavior of Bessel and Neumann functions)

$$\begin{aligned}\int E\Phi_L^{d*}(E^{1/2},\mathbf{r})\Phi_{L'}^d(E'^{1/2},\mathbf{r})d\mathbf{r}&=\lim_{A\rightarrow\infty}\int_0^A E\Phi_L^{d*}(E^{1/2},\mathbf{r})\Phi_{L'}^d(E'^{1/2},\mathbf{r})d\mathbf{r}\\&=\frac{2}{\pi}[C^{d\dagger}(E^{1/2},d)\mathbf{C}^d(E'^{1/2},d)+\mathbf{S}^{d\dagger}(E^{1/2},d)\mathbf{S}^d(E'^{1/2},d)]_{LL'}\lim_{A\rightarrow\infty}\frac{\sin[A(E^{1/2}-E'^{1/2})]}{E^{1/2}-E'^{1/2}}\end{aligned} \tag{25}$$

where we recall that $\lim_{A\rightarrow\infty}[\sin(Ax)/x]=\pi\delta(x)$ as $A\rightarrow\infty$.

Thus we have solved the (integral) eigenvalue problem, Eq. (14), by considering the on-shell representation, Eq. (19), which satisfies Eq. (1) for any choice of the A coefficients and subsequently choosing these coefficients in order to satisfy the boundary conditions contained in Eq. (14). Technically, it means to first find the boundary conditions at the origin, Eq. (17), then to derive the on-shell representation Eq. (19) and finally to find the algebraic system, Eq. (20); similarly, in the case of the scattering states, Eq. (23), we obtain an inhomogeneous linear system which leads to Eq. (24). In other words, Eq. (14) is equivalent to the system of Eqs. (19) and (21), and similarly for the scattering states.

Ultimately, this procedure relies on the fact that the regular solutions $\Phi^d(E^{1/2},\mathbf{r})$ [which are easily found by solving Volterra-type integral equations, Eq. (12)] form an on-shell base for both the bound states and scattering states. Moreover, the coefficients of the expansions of the bound states and scattering states in this base can be found by using boundary conditions and not the scalar product [as is usual in a diagonalization procedure, Eq. (15)].

With the corresponding modifications required by the Bloch periodicity condition, we will follow essentially the same philosophy in converting the Bloch-periodic eigenvalue problem [Eq. (31) below] into an algebraic problem [Eq. (84) below]. Thus, in the next section we find the analogue of Eqs. (17) and (19) for the case of a periodic potential and, after discussing in Sec. IV some particular questions raised by the Bloch periodicity, we find in Sec. V the analog of Eq. (20) and prove its equivalence to the result obtained by the plane-wave diagonalization (which represents the exact result).

III. BLOCH FUNCTION AND ITS BLOCH-PERIODIC PROLONGATION

We recall here some results[16] concerning the prolongation of the Bloch function (with Bloch boundary conditions) and, in view of later developments, proceed to a detailed analysis of its multipole expansion.

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

$$\begin{aligned}\mathbf{r}&=\mathbf{R}+\boldsymbol{\rho}\ ,\\\mathbf{k}&=\mathbf{K}+\boldsymbol{\kappa}\ .\end{aligned} \tag{26}$$

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

$$V=\sum_R\mathcal{V}_\mathbf{R}\ , \tag{27}$$

where

$$\mathcal{V}_\mathbf{R}(\mathbf{r})=\begin{cases}0 & \text{for } r\neq\mathbf{R}+\boldsymbol{\rho}\\ \mathcal{V}(\boldsymbol{\rho}) & \text{for } \mathbf{r}=\mathbf{R}+\boldsymbol{\rho}\ ,\end{cases} \tag{28}$$

and the potential $\mathcal{V}(\rho)$ has an arbitrary range $\alpha \leq \max_{\rho\in\Omega}\rho$ where ρ denotes the modulus $|\boldsymbol{\rho}|$ and, hereafter, r will denote $|\mathbf{r}|$; also, the potential $\mathcal{V}$ is supposed to satisfy the usual regular conditions at the origin.[18] 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, $d\geq 0$, we introduce the potential $V^d(\mathbf{r})$, as defined by

$$V^d(\mathbf{r})=\begin{cases} V(\mathbf{r}) & \text{for } r\leq d \\ 0 & \text{elsewhere}, \end{cases} \tag{29}$$

where $V(\mathbf{r})$ is defined in (27). Obviously, $V^\mu=\mathcal{V}^{\mathrm{MT}}$ denotes the cell potential restricted to the inscribed sphere and zero elsewhere.

With this notation, the Bloch function $\Psi(\boldsymbol{\kappa},E_n,\boldsymbol{\rho})$, $\boldsymbol{\kappa}\in\tilde{\Omega}$, $\boldsymbol{\rho}\in\Omega$ with energy $E_n(\boldsymbol{\kappa})>0$ $(n=0,1,2,\ldots)$ is the solution of the eigenvalue integral equation

$$\Psi(\boldsymbol{\kappa},E,\boldsymbol{\rho})=\frac{1}{\omega}\int_\Omega \sum_{\mathbf{K}} \frac{e^{i(\boldsymbol{\kappa}+\mathbf{K})\cdot(\boldsymbol{\rho}-\boldsymbol{\rho}')}}{E-(\boldsymbol{\kappa}+\mathbf{K})^2} \times \mathcal{V}(\boldsymbol{\rho}')\Psi(\boldsymbol{\kappa},E,\boldsymbol{\rho}')d\boldsymbol{\rho}' \tag{30}$$

or, alternatively,[19]

$$\Psi(\boldsymbol{\kappa},E,\boldsymbol{\rho})=\int_\Omega \sum_{\mathbf{R}} e^{i\boldsymbol{\kappa}\cdot\mathbf{R}} \frac{-1}{4\pi} \frac{\cos(E^{1/2}|\boldsymbol{\rho}-\mathbf{R}-\boldsymbol{\rho}'|)}{|\boldsymbol{\rho}-\mathbf{R}-\boldsymbol{\rho}'|} \times \mathcal{V}(\boldsymbol{\rho}')\Psi(\boldsymbol{\kappa},E,\boldsymbol{\rho}')d\boldsymbol{\rho}' \tag{31}$$

in the Hilbert space $\mathcal{H}(\kappa)$ spanned by the plane waves $(e^{i(\boldsymbol{\kappa}+\mathbf{K})\cdot\boldsymbol{\rho}}/\sqrt{\omega})_{\mathbf{K}}$. [Obviously, the function $\Psi(\boldsymbol{\kappa},E,\boldsymbol{\rho})$, being an eigenfunction, is defined only at $E=E_n$; then when we write $\Psi(\boldsymbol{\kappa},E,\boldsymbol{\rho})$ we do not mean an arbitrary energy, but only $E=E_n$.] Clearly, the eigenfunction of Eq. (30) is a superposition of the type

$$\Psi(\boldsymbol{\kappa},E_n,\boldsymbol{\rho})=\sum_{\mathbf{K}} \frac{e^{i(\boldsymbol{\kappa}+\mathbf{K})\cdot\boldsymbol{\rho}}}{\sqrt{\omega}} a_{\mathbf{K}}(\boldsymbol{\kappa},E_n), \tag{32}$$

which, when introduced in Eq. (30) leads, by using the scalar product in $\mathcal{H}(\boldsymbol{\kappa})$, to the well-known plane-wave diagonalization. Each term in Eq. (32) is Bloch periodic and therefore, the $a_{\mathbf{K}}$ coefficients reflect only the requirement that the function given by Eq. (32) satisfies the Schrödinger equation as a differential equation. Except for the different Hilbert spaces, which are reflected by the use of different Green functions, we recognize here the same problems as in Eqs. (14) and (15), respectively. Similarly to these equations, we want to represent the Bloch function (for reasons to be obvious soon) as a superposition in which each individual term satisfies the Schrödinger equation (as a differential equation) and the coefficients are found by matching the boundary conditions (and hence require computational evaluation). Since the Bloch-periodic Green function in Eq. (31) has a multipole decomposition which comes, essentially, from Eq. (16), we can proceed by using the procedure followed in Eqs. (16)–(22).

Thus we find from Eq. (31) the following boundary condition

$$\Psi(\boldsymbol{\kappa},E_n,\boldsymbol{\rho})\rightarrow \sum_L j_L(E_n^{1/2}(\boldsymbol{\kappa}),\boldsymbol{\rho})A_L(\boldsymbol{\kappa},E_n) \quad \text{as } \rho\rightarrow 0, \tag{33}$$

where we introduced the abbreviations

$$A_L(\boldsymbol{\kappa},E_n)=\frac{\pi E_n^{1/2}(\boldsymbol{\kappa})}{2}\int_\Omega n_L^*(\boldsymbol{\kappa},E_n^{1/2}(\boldsymbol{\kappa}),\boldsymbol{\rho}) \times \mathcal{V}(\boldsymbol{\rho})\Psi(\boldsymbol{\kappa},E_n,\boldsymbol{\rho})d\boldsymbol{\rho}, \tag{34}$$

$$n_L(\boldsymbol{\kappa},E^{1/2},\boldsymbol{\rho})=n_L(E^{1/2},\boldsymbol{\rho})+\mathrm{n}_L(\boldsymbol{\kappa},E^{1/2},\boldsymbol{\rho}+\mathbf{R}), \quad \mathrm{n}_L(\boldsymbol{\kappa},E^{1/2},\boldsymbol{\rho})=\sum_{R\neq 0} e^{-i\boldsymbol{\kappa}\cdot\mathbf{R}} n_L(E^{1/2},\boldsymbol{\rho}+\mathbf{R}), \tag{35}$$

and $j_L(E^{1/2},\mathbf{r})$ denotes, as usual, the spherical Bessel function multiplied with a spherical function and similarly for (the Neumann function) $n_L(E^{1/2},\mathbf{r})$.

Now compare Eqs. (33) and (34) with Eqs. (17) and (18), respectively. They reflect the same philosophy, namely, from the (integral) eigenvalue equation we found the boundary conditions at the origin; only the Neumann function in Eq. (18) is replaced by the "Bloch-periodic Neumann function" defined in Eq. (35), which comes from the Bloch-periodic Green function expressed in Eq. (31). [Or, alternatively, from the fact that Eq. (31) has to be solved in the space $\mathcal{H}(\boldsymbol{\kappa})$, whereas Eq. (14) is solved in the space $L^2(\mathbb{R}^3)$.] Note that the integral in the right-hand side of Eq. (34) makes sense only if the function Ψ belongs to the space $\mathcal{H}(\boldsymbol{\kappa})$. The function defined in Eq. (35) contains information concerning only the geometry of the lattice, exists for any complex energy and, for $\rho\leq \min R$, has the representation

$$n_L(\boldsymbol{\kappa},z,\boldsymbol{\rho})=n_L(z,\boldsymbol{\rho})+\sum_{L'} j_{L'}(z,\boldsymbol{\rho})N_{L'L}(\boldsymbol{\kappa},z), \quad \rho\leq \min\{R\} \tag{36}$$

where $N_{LL'}(\boldsymbol{\kappa},E^{1/2})$ is the usual structure constant.[4,20,21] For those $\boldsymbol{\rho}$ with $\rho\geq\min\{R\}$, the sum in Eq. (36) is not convergent[20] but we can isolate in Eq. (35) a finite number of terms with $R\leq\rho$ (i.e., the nearest and perhaps the next neighbors) and obtain for the remaining (infinite) sum an expression similar to the last term in Eq. (36). Thus the function defined in Eq. (35) exists for any $\boldsymbol{\rho}\in\Omega$, $\rho\neq 0$, and has a ρ^{-l-1} singularity at the origin, whereas the Bessel function is regular at the origin like ρ^l. As an example of the integral which appears in Eq. (34), which is also useful later, we mention the result

$$\int_\Omega n_L^*(\boldsymbol{\kappa},E^{1/2},\boldsymbol{\rho})e^{i(\boldsymbol{\kappa}+\mathbf{K})\cdot\boldsymbol{\rho}}d\boldsymbol{\rho} = \frac{(2\pi)^{3/2}i^l Y_L^*((\boldsymbol{\kappa}+\mathbf{K})/|\boldsymbol{\kappa}+\mathbf{K}|)}{E-(\boldsymbol{\kappa}+\mathbf{K})^2} \times \frac{2}{\pi E^{1/2}}\left[\frac{(\boldsymbol{\kappa}+\mathbf{K})^2}{E}\right]^{l/2} \tag{37}$$

which is easily obtained by considering the action [in

$\mathcal{H}(\kappa)$] of the Bloch-periodic Green function which appears in Eqs. (30) and (31) upon the plane wave and by taking the multipole expansion in the limit $\rho \to 0$.

We are now in a position to see why we chose to solve Eq. (31) along the lines of Eqs. (16) to (22). Since in Eq. (34) the Bloch-periodic boundary conditions were already introduced by means of the function $n(\kappa,E,\rho)$ defined by Eqs. (35) and (36), it is reasonable to use for the Bloch function required in this equation a representation which focuses primarily on satisfying the Schrödinger equation (as a differential equation) and not on the Bloch boundary conditions (which have already been included). In other words, we want in Eq. (34) a representation of the Bloch function as a superposition in which each individual term satisfies the (Schrödinger) differential equation and not the Bloch boundary conditions [whose fulfillment is left to the coefficients of the above superposition, akin to Eq. (19) and not to Eq. (15)]. We now proceed along this line.

Since the Bloch function admits a multipole expansion inside the inscribed sphere,[22] and this expansion is unique, we have, for $\rho \le \mu$, the representation

$$\Psi(\kappa,E_n,\rho)=\sum_L \Phi_L^{\mu}(E_n^{1/2}(\kappa),\rho)A_L(\kappa,E_n), \quad \rho \le \mu \tag{38}$$

where the functions $\Phi_L^{\mu}(E^{1/2},\rho)=\Phi_L^{\mathrm{MT}}(E^{1/2},\rho)$ are the regular solutions, as described by Eqs. (12) for the potential $V^{\mu}=\mathcal{V}^{\mathrm{MT}}$ (in the inscribed sphere) (Ref. 18)

$$\Phi_L^{\mu}(E^{1/2},\rho)=\sum_{L'}[j_{L'}(E,\rho)C_{L'L}^{\mu}(E^{1/2},\rho) + n_{L'}(E^{1/2},\rho)S_{L'L}^{\mu}(E^{1/2},\rho)] \tag{39}$$

Compare Eq. (38) with Eq. (19) and notice the restriction $\rho \le \mu$ which, ultimately, is required by the orthonormality of the spherical functions.[23]

Now the description of the Bloch function as a multipole expansion inside the inscribed sphere has been known for a long time.[3,4,21] The real novelty of Eq. (38), however, is that it was derived from the multipole expansion at the origin, whose coefficients [the $A_L(\kappa,E_n)$] were found to be given by Eq. (34) by means of the decomposition Eq. (16), similar to the case of a finite range potential, Eq. (19). The close similarity between Eqs. (31), (33), (34) and Eqs. (14), (17), (18), respectively, suggests that, provided the Bloch function in Eq. (34) can be expressed in terms of the coefficients $A_L(\kappa,E_n)$, then the eigenvalue equation, Eq. (31), might be transformed into a homogeneous algebraic system for the A coefficients, similar to Eq. (21). The problem then remains to properly express the Bloch function [as an element of the Hilbert space $\mathcal{H}(\kappa)$] in Eq. (34), i.e., within the whole unit cell, not only in the inscribed sphere, in terms of the coefficients $A_L(\kappa,E_n)$.

For this, we recall the prolongation of the Bloch function in any finite sphere.[16] More precisely, we introduce the function $\Psi^d(\kappa,E_n,\mathbf{r})$, defined, according to Eq. (26), for $r=|\rho+\mathbf{R}| \le d$ and for any finite $d \ge \mu$, as the prolongation[23] of the function $\Psi(\kappa,E_n,\rho)$, solution of Eqs. (30) and (31), defined by taking

$$\Psi^d(\kappa,E_n,\rho+\mathbf{R})=e^{i\kappa\cdot\mathbf{R}}\Psi(\kappa,E_n,\rho)\ , \tag{40a}$$

$$\nabla\Psi^d(\kappa,E_n,\rho+\mathbf{R})=e^{i\kappa\cdot\mathbf{R}}\nabla\Psi(\kappa,E_n,\rho)\ , \tag{40b}$$

i.e., with Bloch-periodic boundary conditions.

The function $\Psi^d(\kappa,E_n,\mathbf{r})$, $r \le d$, is given then by the right-hand side of Eq. (30) or (31) with $\rho \to \mathbf{r}$ and $E \to E_n$. As we now have the Bloch function inside the sphere with (finite) radius d, we need to know how translational symmetry operates in this sphere. Clearly, the translation group differs from point to point; for each point $\rho \in \Omega$ there are a finite number $n^d(\rho)$ of translations $\mathbf{R}$ that leave this point inside the sphere with radius d and given as solutions of the (Diophantine) equation

$$|\rho+\mathbf{R}| \le d\ . \tag{41}$$

For fixed d, $n^d(\rho)$ is a piecewise constant function, monotonically increasing with d, and having the properties

$$\begin{aligned} &n^d(\rho+\mathbf{R})=n^d(\rho) \quad \text{for} \quad |\rho+\mathbf{R}| \le d\ , \\ &n^{\mu}(\rho)=1\ . \end{aligned} \tag{42}$$

As $d \to \infty$, it has the limit

$$\lim_{d\to\infty} n^d(\rho)=N_{\Omega}^d=N_{\Omega} \to \infty \tag{43}$$

independent of ρ, where N_{Ω} is the number of cells in the crystal.

We now seek to find a relation between the function $\Psi^d(\kappa,E_n,\mathbf{r})$ and the Bloch function inside the inscribed sphere, where we have the multipole expansion, Eqs. (38) and (39). To accomplish this, we use the fact that the function $\Psi^d(\kappa,E_n,\mathbf{r})$ has a multipole expansion [from Ref. 23 and Eqs. (31), (40), and (16)]

$$\Psi^d(\kappa,E_n,\mathbf{r})=\sum_L Y_L(\hat{\mathbf{r}})\psi_L^d(\kappa,E_n,r) \tag{44}$$

where the functions $\psi_L^d(\kappa,E_n,r)$ are easily seen [by taking $\rho \to \mathbf{r}$ in Eq. (31), commuting a finite subsum with the integral and using Eq. (16)] to satisfy the coupled channel equation [compare with Eqs. (9) and (12c)]

$$\psi_L^d(\kappa,E,r)=j_l(E^{1/2}r)X_L^d+n_l(E^{1/2}r)Z_L^d - \frac{\pi E^{1/2}}{2}\int_r^d W_l(E^{1/2},r,r') \times \sum_{L'} V_{LL'}^d(r')\psi_{L'}^d(\kappa,E,r')r'^2dr' \tag{45}$$

at $E=E_n$ and $\mu \le r \le d$. In Eq. (45), the function $W_l(E^{1/2},r,r')$ and the matrix elements $V_{LL'}^d(r')$ are defined in Eq. (11) and (4), respectively; the coefficients X_L^d and Z_L^d (whose dependence on $\bar{\kappa}$ and E was omitted) are given by

$$X_L^d = A_L(\kappa,E) - \frac{\pi E^{1/2}}{2}\int_{r\le d} n_L^*(E^{1/2},\mathbf{r}) \times V^d(\mathbf{r})\Psi^d(\kappa,E,\mathbf{r})d\mathbf{r}\ ,$$
$$Z_L^d = \frac{\pi E^{1/2}}{2}\int_{r\le d} j_L^*(E^{1/2},\mathbf{r})V^d(\mathbf{r})\Psi^d(\kappa,E,\mathbf{r})d\mathbf{r} \quad (46)$$

at $E=E_n$. The system (45) can be solved in terms of the functions $\Phi_L^{d,\lambda}(E^{1/2},\mathbf{r})$ defined in Eqs. (13) for the potential $V^d(\mathbf{r})$ defined in[18] Eq. (29)

$$\psi_{L'}^{d,\lambda}(\kappa,E_n,r) = \sum_L [\phi_{L'L}^{d,j}(E_n^{1/2}(\kappa),r)X_L^d + \phi_{L'L}^{d,n}(E_n^{1/2}(\kappa),r)Z_L^d] \quad (47)$$

which, when introduced, together with Eq. (39), into Eqs. (46), results in a linear system connecting the quantities $A_L(\kappa,E_n)$, X_L^d, and Z_L^d

$$\sum_L C_{L'L}^{\mu}(E^{1/2},\mu)A_L(\kappa,E^{1/2}) = \sum_L [C_{L'L}^{d,j}(E^{1/2},\mu)X_L^d + C_{L'L}^{d,n}(E^{1/2},\mu)Z_L^d]\ ,$$
$$\sum_L S_{L'L}^{\mu}(E^{1/2},\mu)A_L(\kappa,E^{1/2}) = \sum_L [S_{L'L}^{d,j}(E^{1/2},\mu)X_L^d + S_{L'L}^{d,n}(E^{1/2},\mu)Z_L^d]\ , \quad (48)$$

at $E=E_n$. From Eq. (48) we learn [by using Eq. (8)] that the function defined in Eq. (40) for $r\le d$ and expressed by Eqs. (44)–(47) for $\mu\le r\le d$ matches (in both the function and the normal derivative) the superposition Eq. (38) on the sphere with radius μ. We therefore conclude that for any $r\le d$ (i.e., not only for $r\le\mu$), the function $\Psi^d(\kappa,E_n,\mathbf{r})$ is given by [cf. Eq. (19)]

$$\Psi^d(\kappa,E_n,\mathbf{r}) = \sum_L \Phi_L^d(E_n^{1/2}(\kappa),\mathbf{r})A_L(\kappa,E_n),\quad r\le d \quad (49)$$

where the functions $\Phi_L^d(E,\mathbf{r})$ are given by Eq. (12) for the potential defined in Eq. (29). The coefficients $A_L(\kappa,E_n)$ are independent of d and coincide with those defined in Eq. (34) and used in Eq. (38). [In fact, this was the reason for introducing[23] the prolongation defined by Eq. (40)]. Note that the functions $\Psi^d(\kappa,E_n,\mathbf{r})$ can be given a prolongation in the whole space by removing from Eq. (49) the condition $r\le d$ [for $r\ge d$, where the potential V^d is zero, the functions $\Phi_L^d(E,\mathbf{r})$ are represented from Eqs. (7) and (12), by a superposition of Bessel and Neumann functions]. This prolongation, however, coincides with the Bloch function *only* inside the sphere with radius d; in the limit $d=\infty$, however, it coincides with the Bloch function extended to the whole space.

Now Eq. (49) says that the function $\Psi^d(\kappa,E_n,\mathbf{r})$, which is the Bloch-periodic extension in the sphere $r\le d$ of the Bloch function defined by Eq. (31), is a superposition of the regular solutions, Eq. (12), with potential defined in Eq. (29). These regular solutions are clearly not Bloch periodic[24] [although they carry some information about both the translational and point-group symmetries of the periodic potential, Eq. (27), by means of the matrix elements[25] defined in Eq. (4)]. Obviously, the restriction of Eq. (49) for $\mathbf{r}=\boldsymbol{\rho}\in\Omega$ gives the values of the Bloch function inside the unit cell

$$\Psi(\kappa,E_n,\boldsymbol{\rho}) = \sum_L \Phi_L^d(E_n^{1/2}(\kappa),\boldsymbol{\rho})A_L(\kappa,E_n)\ , \quad (50a)$$

where, although the individual terms are not Bloch periodic, the sum belongs to the Hilbert space $\mathcal{H}(\kappa)$. In fact, Eq. (50a) implies only the function $\Phi_L^{\mathrm{circ}}(E_n^{1/2},\mathbf{r})$ corresponding to the radius of the circumscribing sphere

$$\Psi(\kappa,E_n,\boldsymbol{\rho}) = \sum_L \Phi_L^{\mathrm{circ}}(E_n^{1/2}(\kappa),\boldsymbol{\rho})A_L(\kappa,E_n)\ , \quad (50b)$$

because the regular solution $\Phi_L^d(E_n^{1/2},\mathbf{r})$ has, from Eqs. (29) and (12), the obvious property

$$\Phi_L^d(E_n^{1/2},\mathbf{r}) = \Phi_L^{d'}(E_n^{1/2},\mathbf{r}) \quad \text{for } r\le\min(d,d') \quad (51)$$

However, Eq. (50) does not represent the multipole expansion of the Bloch function (which, in fact, does not exist) but the multipole expansion of one of its prolongations, namely that defined by Eq. (40).[23] Finally, it is worth mentioning that Eqs. (33)–(50) can be illustrated in a soluble model, namely a constant periodic potential.[16]

So far we have seen that the Bloch-periodic extension $\Psi^d(\kappa,E_n,\mathbf{r})$ of the Bloch function $\Psi(\kappa,E_n,\boldsymbol{\rho})$ can be represented, in complete analogy to Eq. (19), as an on-shell superposition, Eq. (49), of the regular solutions $\Phi_L^d(E_n^{1/2},\mathbf{r})$ corresponding to the potential V^d which are not Bloch periodic.[24] Accordingly, the Bloch function, when restricted to the unit cell, can be represented[26] as given by Eq. (50b).

How can we use this information in order to compute the band structure and wave functions for a periodic potential? Clearly, by using Eqs. (49) and (50), not only in Eq. (34) but in *both* Eqs. (34) and (40), in order to obtain a homogeneous linear system for the coefficients $A_L(\kappa,E_n)$. The point here is to properly describe the Bloch function, as an element of the space $\mathcal{H}(\kappa)$, in terms of the $A_L(\kappa,E_n)$ coefficients, where we recall that the sum in Eq. (50) is Bloch periodic in spite of the fact that each individual term does not have this property. This point pertains to the description of the Bloch function, as an element of the Hilbert space of Bloch-periodic functions, by using multipole expansions. Before proceeding along this line in the next two sections, let us first obtain additional insight into the nature of Eqs. (49) and (50) by comparing the ways in which the coefficients $a_{\mathbf{K}}$ of the usual plane-wave expansion, Eq. (32), and the coefficients $A_L(\kappa,E_n)$, Eqs. (49) and (50), carry information about the Bloch function $\Psi(\kappa,E_n,\boldsymbol{\rho})$ defined by Eq. (31).

It is easy to see that knowing a set of numbers $a_{\bar{K}}$ in Eq. (32) fully determines the Bloch function (i.e., both the energy and the analytical form), whereas knowing the numbers A_L in Eqs. (49) and (50) needs to be supplemented with a knowledge of the energy $E_n(\kappa)$ which determines the function $\Phi_L^d(E_n^{1/2},\boldsymbol{\rho})$. This originates in the fact that Eq. (32) is a superposition in the Hilbert

space $\mathcal{H}(\kappa)$, spanned by the $(e^{i(\kappa+\mathbf{K})\cdot\rho})_{\mathbf{K}}$, whereas Eqs. (49) and (50) were determined as superpositions in the linear space of the regular solutions of Eq. (1). More insight can be obtained by using variational principle language[4] according to which the eigenvalue problem, Eq. (30) or (31), is equivalent to finding the minimum of $[H^{\text{Bloch}}(\kappa)-E]$ or, alternatively of the Kohn-Rostoker functional, in the class of Bloch periodic functions, i.e., in the Hilbert space $\mathcal{H}(\kappa)$. Then, since a superposition of the $(e^{i(\kappa+\mathbf{K})\cdot\rho})_{\mathbf{K}}$ is already Bloch periodic, the coefficients a_K in Eq. (32) are subject only to the minimization of $[H^{\text{Bloch}}(\kappa)-E]$ or, alternatively, of the Kohn-Rostoker functional. On the contrary, a superposition of the $\Phi_L^d(E^{1/2},\mathbf{r})$, solutions of Eq. (1) with potential Eq. (29) at arbitrary E, with arbitrary coefficients A_L is not granted to be Bloch periodic; such a superposition describes a regular solution of the Schrödinger equation (as a differential equation only), and hence it describes not only Bloch-periodic functions but the bound states and scattering states (of the potential V^d) as well. It is therefore incorrect to take the minimum of $[H^{\text{Bloch}}(\kappa)-E]$ or of the Kohn-Rostoker functional in the class of such superpositions (because this class of functions is larger than the class of Bloch-periodic functions).

More precisely, in a variational principle approach, we have to both (i), *restrict* the coefficients A_L by means of Eq. (40) (in order to achieve Bloch periodicity) and (ii) *minimize* the above functionals. Thus the coefficients A_L in the right-hand side of Eqs. (49) and (50) with arbitrary E are not only subject to the minimization of the above functionals but are also subject to some supplementary conditions as well, in order to assure the Bloch periodicity expressed by Eqs. (40). Surely, one can forget about the last requirement and deal with the coefficients A_L as they satisfy only the above minimization condition, which means to break (partially) the Bloch periodicity. [It is only partially broken, because the Bloch boundary conditions are also included in the functions $n(\kappa,E^{1/2},\rho)$ which are not affected by the above procedure. Aside from the present proof and the claim to be exact,[9] this is equivalent to the procedure used in Ref. 9.] In this approximation, a superposition as given by the right-hand side of Eq. (50) at an arbitrary energy will satisfy the (Bloch periodic) Schrödinger equation at any *interior* point of Ω, but not on the boundary. Thus one can equally choose a superposition of functions which satisfy Eq. (1) with V^d replaced by the cell potential $V(\rho)$. (Motivated by other reasons but also presented as an exact result, such a superposition was introduced years ago;[6] subsequently, the need for "near-field corrections" was pointed out.[7,8,12]) Also, although arrived at in a completely different approach, this type of superposition has been recently considered as an approximation.[11]

The difficult point with the multipole superpositions. Eqs. (49) and (50), consists in the fact that each term does not belong to the Hilbert space $\mathcal{H}(\bar{\kappa})$ spanned by the functions $(e^{i(\kappa+\mathbf{K})\cdot\rho})_{\mathbf{K}}$, but their sum represents such an element. As a way of circumventing this difficulty, we may use [in the spirit of the augmented-plane-wave (APW) method] a mixed representation[22,23]

$$\Psi(\kappa,E_n,\rho)=\sum_L \Phi_L^{\text{MT}}(E_n^{1/2}(\kappa),\rho)A_L(\kappa,E_n),\quad \rho\le\mu \tag{52a}$$

for those points which belong to the inscribed sphere S^{MT}, and

$$\Psi(\kappa,E_n,\rho)=\sum_{\mathbf{K}} \frac{e^{i(\kappa+\mathbf{K})\cdot\rho}}{\sqrt{\omega}} a_{\mathbf{K}}(\kappa,E_n),\quad \rho\in\Omega,\ \rho\ge\mu \tag{52b}$$

for the rest of the unit cell hereafter denoted by $\Omega\setminus S^{\text{MT}}$. Here, the two sets of coefficients $a_{\mathbf{K}}(\kappa,E_n)$ and $A_L(\kappa,E_n)$ are connected by a matching condition for both function and derivative on the inscribed sphere. Since there are two independent conditions, one set of coefficients, say $a_{\mathbf{K}}$, can be eliminated and hence we obtain a condition for the A coefficients. By construction, this condition expresses the fact that the Bloch function represented by Eq. (52a) inside the inscribed sphere, satisfies, in the rest of the unit cell, the Bloch-periodic Schrödinger equation. We are then left to impose upon the function, Eq. (52), only the condition of satisfying the Bloch-periodic Schrödinger equation inside the inscribed sphere, i.e., to impose Eq. (34). This results in a homogeneous system of equations

$$\sum_L \left[\delta_{L'L}-\frac{\pi E^{1/2}}{2}\int_{S^{\text{MT}}} n_{L'}^*(\kappa,E^{1/2},\rho)\mathcal{V}(\rho)\Phi_L^{\text{MT}}(E^{1/2},\rho)\right]A_L(\kappa) + \sum_{\mathbf{K}}\frac{\pi E^{1/2}}{2}\int_{\Omega\setminus S^{\text{MT}}} n_{L'}^*(\kappa,E^{1/2},\rho)\mathcal{V}(\rho)\frac{e^{i(\kappa+\mathbf{K})\cdot\rho}}{\sqrt{\omega}}d\rho\, a_{\mathbf{K}}(\kappa)=0 \tag{53a}$$

which, together with the matching condition discussed above, uniquely determine the eigenenergies E and the A coefficients. In the muffin-tin case, Eq. (53a) contains only the A coefficients

$$\sum_L \left[\delta_{L'L}-\frac{\pi E^{1/2}}{2}\int_{S^{\text{MT}}} n_{L'}^*(\kappa,E^{1/2},\rho)\mathcal{V}(\rho)\times\Phi_L^{\text{MT}}(E^{1/2},\rho)d\rho\right]A_L(\kappa)=0\ . \tag{53b}$$

Thus by using Eqs. (36) and (51), we have rediscovered the KKR equation which, in the present context, expresses the fact that the Bloch function represented by Eq. (52a) for $\rho\le\mu$ satisfies the Bloch-periodic Schrödinger equation but *only* inside the inscribed sphere. Hence, Eq. (53b) for $E=E_n(\kappa)$ appears to represent only a necessary condition for the A coefficients which, in view of the equivalence with Eq. (30), has to be supplemented with the (above discussed) relation among the A coefficients expressing the matching between the representations given in Eqs. (52a) and

(52b). Obviously, Eq. (53b) might represent not only a necessary but also a sufficient condition; however, until this is proven, we have to consider Eq. (53b), by construction, only as a necessary condition for the A coefficients.

Coming back to the point that each term in Eq. (50) is not Bloch periodic but their sum belongs to the space of Bloch-periodic functions, we have yet another way to circumvent this difficulty. Actually, in the limit $d=\infty$, Eq. (49) provides (by construction) the Bloch function in the whole space. Hence, the Bloch function in the unit cell [which appears in Eq. (34)] can be obtained by a folding back procedure of the prolongation Eq. (49) for $d=\infty$; thus the on-shell superposition, Eq. (50), can be converted into a superposition in the space $\mathcal{H}(\kappa)$, which superposition still preserves the on-shell feature but in a more general, distribution sense. This will be discussed in the next section.

IV. BLOCH FUNCTION AND ON-SHELL PERIODIC ORBITALS

By using Eq. (49) and Eqs. (40) to (42) in the form

$$\sum_L \Phi_L^d(E_n^{1/2}(\kappa),\mathbf{r})A_l(\kappa,E_n)=\Psi^d(\kappa,E_n,\mathbf{r}) =e^{-i\kappa\cdot\mathbf{R}}\Psi^d(\kappa,E_n,\mathbf{r}+\mathbf{R}) \tag{54}$$

for each R with $|\mathbf{r}+\mathbf{R}|\le d$ [whose number is $n^d(\mathbf{r})$], Eq. (50) can be written as

$$\Psi^d(\kappa,E_n,\rho)=\sum_L \tilde{\Phi}_L^d(\kappa,E_n^{1/2}(\kappa),\rho)A_l(\kappa,E_n)\ , \tag{55}$$

where we introduced the functions

$$\tilde{\Phi}_L^d(\kappa,E^{1/2},\rho)=\frac{1}{n^d(\rho)}\Phi_L^d(\kappa,E^{1/2},\rho) \tag{56a}$$

and

$$\Phi_L^d(\kappa,E^{1/2},\rho)=\sum_{\mathbf{R},\ |\rho+\mathbf{R}|\le d} e^{-i\kappa\cdot\mathbf{R}}\Phi_L^d(E^{1/2},\rho+\mathbf{R}) \tag{56b}$$

defined at $E=E_n(\kappa)$. Note that their energy (at a fixed $\kappa\in\tilde{\Omega}$) is allowed to take only the values E_n, as in the Bloch function. This naturally raises the question, what would be the result if the folding procedure, Eq. (56), with a fixed κ is applied to a regular solution at $E\neq E_n$. But before considering this question, we first obtain more insight into the meaning of Eqs. (54) and (55). Obviously, Eq. (55) represents a step forward in transforming Eq. (50) into a superposition in the Hilbert space $\mathcal{H}(\bar{\kappa})$. Actually, the $\tilde{\Phi}_L^d(\kappa,E^{1/2},\rho)$ (at any E) satisfy Eq. (40a) but, apparently, are discontinuous [both $\Phi_L^d(\kappa,E^{1/2},\rho)$ and $n^d(\rho)$ are discontinuous]. Thus the superposition Eq. (55) is not (yet) a superposition of Bloch-periodic functions, but for any required accuracy one can find a d for which $\tilde{\Phi}_L^d(\kappa,E^{1/2},\rho)$ becomes continuous and hence Bloch periodic [i.e., $\tilde{\Phi}_L^d(\kappa,E^{1/2},\rho)$ exactly satisfies Eq. (40a) and within any accuracy Eq. (40b)]. This can be seen by rewriting Eq. (56a) in the form

$$\tilde{\Phi}_L^d(\kappa,E^{1/2},\rho)=\Phi_L^{\mathrm{circ}}(E,\rho)+\varphi_L^d(\kappa,E^{1/2},\rho)\ , \tag{57a}$$

where we introduced [use was made of Eq. (51)]

$$\varphi_L^d(\kappa,E^{1/2},\rho)=\frac{1}{n^d(\rho)}\sum_{\mathbf{R},\ |\rho+\mathbf{R}|\le d}[e^{-i\kappa\cdot\mathbf{R}}\Phi_L^d(E^{1/2},(\rho+\mathbf{R}))-\Phi_L^{\mathrm{circ}}(E^{1/2},\rho)]\ , \tag{57b}$$

and taking for an arbitrary d two points $\rho,\rho'\in\Omega$ that are close enough but with $n^d(\rho)-n^d(\rho')\ge 1$, and finally using the fact that, according to Eq. (43), the limit $\lim_{d\to\infty} n^d(\rho)$ is independent of ρ. [The relations (54)–(57) are illustrated in Ref. 16 for the soluble case of a constant periodic potential.]

Now as stated above, the functions defined in Eq. (56) are not Bloch periodic for they are discontinuous. However, these functions satisfy Eq. (40a), and the larger the value of d, the smaller the discontinuities. Then we might expect that in the limit $d=\infty$ the functions defined in Eq. (56) become continuous and hence Bloch periodic. We now focus on this limit. Clearly, the existence of Eqs. (55) and (56) in the limit $d=\infty$, i.e.,

$$\Psi(\kappa,E_n,\rho)=\sum_L \tilde{\Phi}_L(\kappa,E_n^{1/2}(\kappa),\rho)A_L(\kappa,E_n)\ , \tag{58}$$

$$\tilde{\Phi}_L(\kappa,E_n^{1/2},\rho)=\lim\left[\frac{1}{N_\Omega}\Phi_L(\kappa,E_n^{1/2},\rho)\right]\quad \text{as } N_\Omega\to\infty\ , \tag{59a}$$

$$\Phi_L(\kappa,E_n^{1/2},\rho)=\sum_{\mathbf{R}} e^{-i\kappa\cdot\mathbf{R}}\Phi_L(E_n^{1/2},\rho+\mathbf{R})\ , \tag{59b}$$

should be determined by the periodicity of the potential V^d, defined in Eq. (29). Thus the problem is to show that the behavior of the regular solutions given by Eq. (12) with potential Eq. (29) at $E=E_n$ justifies the limits Eqs. (58) and (59). More precisely, the problem is to find the limits, Eq. (59), by using only Eq. (12) with potential Eq. (29) at $E=E_n$ and thus to rediscover Eq. (58) without resorting to Eqs. (40), (42), (54), and (55). Apparently, the difficulty here consists in finding the meaning of the limit

$$\Phi_L(E^{1/2},\mathbf{r})=\lim_{d\to\infty}\Phi_L^d(E^{1/2},\mathbf{r})\ , \tag{60}$$

where the regular functions $\Phi_L^d(E^{1/2},\mathbf{r})$ are defined in Eq. (12) with potential Eq. (29); for the sake of generality, we consider an arbitrary E. [This leads to considering the folding procedure Eq. (56) for a certain κ with an energy, as already stated, different from the Bloch energies at the point κ, and hence to find the meaning of this folding procedure.] This is a rather delicate point, and,

in order to obtain insight, we first recall the soluble case of a positive constant periodic potential[27] for which

$$\frac{e^{i(\kappa+\mathbf{K})\cdot\mathbf{r}}}{\sqrt{\omega}}=\sqrt{\tilde{\omega}}\sum_L j_L(|\kappa+\mathbf{K}|,\mathbf{r})\times i^l Y_L^*((\kappa+\mathbf{K})/|\kappa+\mathbf{K}|)\,, \tag{61a}$$

$$\Phi_L(E^{1/2},\mathbf{r})=\left[\frac{E}{E-V}\right]^{l/2} j_L((E-V)^{1/2},\mathbf{r})\,, \tag{61b}$$

where, by using Eq. (37), the A_L coefficients are easily seen to verify their general definition, Eq. (34). By using translational properties of the Bessel functions,[20] Eqs. (61) are easily shown[16] to result in

$$\tilde{\Phi}_L(\kappa,E^{1/2},\boldsymbol{\rho})=\lim_{N_\Omega\to\infty}\frac{1}{N_\Omega}\Phi_L(\kappa,E^{1/2},\boldsymbol{\rho})\,, \tag{62a}$$

$$\Phi_L(\kappa,E^{1/2},\boldsymbol{\rho})=\sum_{\mathbf{K}}\frac{e^{i(\kappa+\mathbf{K})\cdot\boldsymbol{\rho}}}{\sqrt{\omega}}\left[\frac{\delta((E-V)^{1/2}-|\kappa+\mathbf{K}|)}{E-V}\sqrt{\tilde{\omega}}\left[\frac{V+(\kappa+\mathbf{K})^2}{(\kappa+\mathbf{K})^2}\right]^{l/2} i^{-l}Y_L((\kappa+\mathbf{K})/|\kappa+\mathbf{K}|)\right]. \tag{62b}$$

Thus, by using the relations[28]

$$\begin{aligned}&\int_{\tilde{\Omega}} e^{i\kappa\cdot\mathbf{R}}d\kappa=\tilde{\omega}\delta_{\mathbf{R}}\,,\\ &\sum_{\mathbf{R}} e^{-i\kappa\cdot\mathbf{R}}=\tilde{\omega}\sum_{\mathbf{K}}\delta(\kappa-\mathbf{K})\,,\\ &\lim_{N_\Omega\to\infty}\left[\frac{1}{N_\Omega}\sum_{\mathbf{R}} e^{-i(\kappa-\kappa')\cdot\mathbf{R}}\right]=\begin{cases}1 & \text{if } \kappa=\kappa'\\ 0 & \text{otherwise}\,,\end{cases}\end{aligned} \tag{63}$$

and the decomposition of the δ function in spherical coordinates, we find that the limits Eq. (59) exist in the sense

$$\int_{\tilde{\Omega}} e^{i\kappa\cdot R}\Phi_L(\kappa,E^{1/2},\boldsymbol{\rho})d\kappa=\tilde{\omega}\left[\frac{E}{E-V}\right]^{l/2} j_L((E-V)^{1/2},\boldsymbol{\rho}+\mathbf{R})\,, \tag{64a}$$

$$\sum_L\tilde{\Phi}_L(\kappa,E^{1/2},\boldsymbol{\rho})\left[\sqrt{\tilde{\omega}}\left[\frac{(\kappa+\mathbf{K})^2}{V+(\kappa+\mathbf{K})^2}\right]^{l/2} i^l Y_L^*((\kappa+\mathbf{K})/|\kappa+\mathbf{K}|)\right]=\begin{cases}\dfrac{e^{i(\kappa+\mathbf{K})\cdot\boldsymbol{\rho}}}{\sqrt{\omega}} & \text{if } E=V+(\kappa+\mathbf{K})^2\\ 0 & \text{otherwise}\,,\end{cases} \tag{64b}$$

and hence we have rediscovered Eq. (58). (There are, of course, other properties as well but we confine ourselves here to only those needed for the band-structure equation.) Essentially, we have seen in this example that, in the limit $d=\infty$, the function $\tilde{\Phi}_L^d(\kappa,E^{1/2},\boldsymbol{\rho})$ becomes a superposition, Eq. (62b), of the corresponding Bloch functions, where the coefficients are not numbers but rather distributions which exist in the sense of Eq. (64); also, the energy dependence appears only by means of a δ function. Thus in the case of a constant periodic potential, the meaning of the folding procedure, Eq. (59), can be summarized as follows: the regular solution, Eq. (12) with potential Eq. (29), when folded according to Eq. (56), will select in the limit $d=\infty$ and in the sense of Eq. (64) only the Bloch energies.[29] In other words, the $\tilde{\Phi}_L(\kappa,E^{1/2},\boldsymbol{\rho})$ are Bloch periodic in the sense of Eq. (62) and they represent, in the sense of Eq. (64), an on-shell base for the Bloch functions defined by Eq. (31). Taking this particular result as a hint, we now focus on the case of a general periodic potential.

In this case, a complete analysis of the limit Eq. (60) pertains to the theory of differential equations with periodic coefficients[2] and, in fact, consists in analyzing the Hamiltonian [acting in $L^2(\mathbb{R}^3)$]

$$H^d=-\Delta+V^d \tag{65}$$

when $d\to\infty$. (A soluble model, Kronnig-Penney with δ functions, can be found in Grossman *et al.*[1]) Here, we confine ourselves only to those properties which give sense to the folding procedure Eqs. (56) and (59). Thus we notice [from the normalization, Eq. (25) and theorem XIII 98 in Reed and Simon[1]] that for any finite d, irrespective of E, we have the expansion

$$\Phi_L^d(E^{1/2},\mathbf{r})=\sum_n\int_{\tilde{\Omega}} d\kappa\,\Psi(\kappa,E_n,\mathbf{r})\hat{\Phi}_L^d(\kappa,E_n,E^{1/2})\,, \tag{66}$$

where the coefficients are given by

$$\hat{\Phi}_L^d(\kappa,E_n,E^{1/2})=\int_{\mathbb{R}^3}\Psi^*(\kappa,E_n,\mathbf{r})\Phi_L^d(E^{1/2},\mathbf{r})d\mathbf{r} \tag{67}$$

and have the property

$$\int_{\mathbb{R}^3}|\Phi_L^d(E^{1/2},\mathbf{r})|^2 d\mathbf{r}=\sum_n\int_{\tilde{\Omega}} d\kappa\,|\hat{\Phi}_L^d(\kappa,E_n,E^{1/2})|^2\,. \tag{68}$$

In Eqs. (67)–(68), $\Psi(\kappa,E_n,\mathbf{r})$ represents the (Bloch periodic) prolongation, Eq. (40), of the Bloch function $\Psi(\kappa,E_n,\boldsymbol{\rho})$ defined by Eq. (30) or (31). Also, from Eqs. (12) and (49) we find

$$\sum_L C^d_{L'L}(E^{1/2},d)A_L(\kappa,E_n)$$
$$= A_{L'}(\kappa,E_n) - \frac{\pi E_n^{1/2}}{2}\int_\Omega n^{d*}_{L'}(\kappa,E_n^{1/2},\rho)\mathcal{V}(\rho)$$
$$\times\Psi(\kappa,E_n,\rho)d\rho \tag{69}$$

where $n^d_L(\kappa,E^{1/2},\rho)$ denotes the function

$$n^d_L(\kappa,E^{1/2},\rho)=\sum_{\mathbf{R},\,|\rho+\mathbf{R}|\le d} e^{-i\kappa\cdot\mathbf{R}} n_L(E^{1/2},\rho+\mathbf{R}) , \tag{70}$$

which, in the limit $d=\infty$, becomes the function $n_L(\kappa,E^{1/2}\rho)$ given in Eq. (35). Then in the limit $d=\infty$, we find, by using Eq. (34), that the right-hand side of Eq. (69) becomes zero. Since [from Eq. (35)] the coefficients $A_L(\kappa,E_n)$ are different from zero, it follows that

$$\lim_{d\to\infty}\det C^d(E_n^{1/2}(\kappa),d)=0 . \tag{71}$$

Hence we have shown that the Bloch energies represent the limit $d=\infty$ of the bound-state energies, Eq. (22), of the Hamiltonian H^d defined by Eq. (65).[30] Thus from theorem XIII 98 in Reed and Simon,[1] it follows that the expansion Eq. (66) at a Bloch energy $E=E_n(\kappa)$ with n and κ arbitrary, has a limit when $d\to\infty$ and, moreover, this limit appears to be an on-shell superposition.[31] [That is, when $d\to\infty$ the bound states of Eq. (65) at an energy $E^d_{\text{bound}}\to E_n(\kappa)$ as $d\to\infty$ become less and less bounded and, in the limit $d=\infty$, they appear to be a superposition of the Bloch functions (with various κ) having the same energy as the limit just given.]

To find this on-shell superposition, we introduce[1] the Fourier transform

$$\Phi^d_L(E^{1/2},\mathbf{r})=\int_{\mathbf{R}^3}\frac{e^{i\mathbf{p}\cdot\mathbf{r}}}{(2\pi)^{3/2}}\hat{\Phi}^d_L(E^{1/2},\mathbf{p})d\mathbf{p} , \tag{72a}$$

$$(E-p^2)\hat{\Phi}^d_L(E^{1/2},\mathbf{p})=\int_{\mathbf{R}^3}\hat{V}^d(\mathbf{p}-\mathbf{p}')\hat{\Phi}^d_L(E^{1/2},\mathbf{p})d\mathbf{p}' , \tag{72b}$$

$$\int_{\mathbf{R}^3} i^l\left[\frac{p}{E^{1/2}}\right]^l Y^*_L(\hat{\mathbf{p}})\hat{\Phi}^d_{L'}(E^{1/2},\mathbf{p})d\mathbf{p}=\delta_{LL'} . \tag{72c}$$

Hereafter, the limit $d\to\infty$ is defined by removing the superscript d, i.e., $\hat{\Phi}_L(E^{1/2},\mathbf{p})=\lim_{d\to\infty}\hat{\Phi}^d_L(E^{1/2},\mathbf{p})$. Since the Fourier transform of the periodic potential, Eq. (27), is given by

$$\hat{V}(\mathbf{p})=\sum_{\mathbf{K}}\delta(\mathbf{p}-\mathbf{K})\mathcal{V}_{\mathbf{K}} , \tag{73a}$$

$$\mathcal{V}_{\mathbf{K}}=\int_\Omega\frac{e^{-i\mathbf{K}\cdot\bar{\rho}}}{\omega}\mathcal{V}(\rho)d\rho , \tag{73b}$$

we find the limit $d=\infty$ of Eq. (72b) in the form

$$(E-p^2)\hat{\Phi}_L(E^{1/2},\mathbf{p})=\sum_{\mathbf{K}}\mathcal{V}_{\mathbf{K}}\hat{\Phi}_L(E^{1/2},\mathbf{p}-\mathbf{K}) , \tag{74}$$

which further becomes [from Eqs. (26) and (73b)]

$$[E-(\kappa+\mathbf{K})^2]\hat{\Phi}_L(E^{1/2},\kappa+\mathbf{K})$$
$$=\sum_{\mathbf{K}'}\mathcal{V}_{\mathbf{K}-\mathbf{K}'}\hat{\Phi}_L(E^{1/2},\kappa+\mathbf{K}') , \tag{75}$$

where κ is arbitrarily chosen in $\tilde{\Omega}$. From Eq. (75) we learn that in the limit $d=\infty$, the Fourier transform $\hat{\Phi}_L(E^{1/2},\mathbf{p})$ has a very particular form: for each $\kappa\in\tilde{\Omega}$, the components with $\mathbf{p}=\kappa+\mathbf{K}$ are independent of the components with $\mathbf{p}'=\kappa'+\mathbf{K}'$. More than that, Eq. (75) looks very familiar: if E happens to be an eigenvalue corresponding to the wave vector κ, i.e., $E=E_n(\kappa)$, then the solutions $a_{\mathbf{K}}(\kappa,E_n)$ of

$$[E_n(\kappa)-(\kappa+\mathbf{K})^2]a_{\mathbf{K}}=\sum_{\mathbf{K}'}\mathcal{V}_{\mathbf{K}-\mathbf{K}'}a_{\mathbf{K}'} \tag{76}$$

are numbers having the property $\sum_{\mathbf{K}}|a_{\mathbf{K}}(\kappa,E_n)|^2<\infty$; they give the Bloch function as a superposition, Eq. (32), in the Hilbert space $\mathcal{H}(\kappa)$, spanned by the plane waves $(e^{i(\kappa+\mathbf{K})\cdot\rho})_{\mathbf{K}}$. If the energy E in Eq. (76) does not represent an eigenvalue then this equation has only the trivial (zero) solution. Thus by using the definition of the δ function,[31] we have, for $E=E_{n'}(\kappa')$ (with arbitrary n' and κ')

$$\Phi_L(E^{1/2},\mathbf{r})=\int_{\tilde{\Omega}}d\kappa\sum_n\Psi(\kappa,E_n,\mathbf{r})$$
$$\times\delta(E-E_n(\kappa))\mathcal{A}_L(\kappa,E_n) \tag{77}$$

where the coefficients $\mathcal{A}_L(\kappa,E_n)$ are determined from the boundary conditions Eqs. (72c)

$$\int_{\tilde{\Omega}}d\kappa\sum_n A_{L'}(\kappa,E_n)\delta(E-E_n(\kappa))\mathcal{A}_L(\kappa,E_n)=\delta_{LL'} \tag{78}$$

and use was made of Eqs. (33) and (32). From Eq. (77) we learn that the function $\Phi_L(E^{1/2},\mathbf{r})$ can be represented as a superposition of the Bloch functions with various κ but having the same energy, i.e., an on-shell superposition, where the coefficients are obtained from the boundary conditions at the origin. By now introducing Eq. (78) into Eq. (58) and by using the normalization of Bloch functions (in the whole space) and Eq. (63), one obtains

$$\lim_{N_\Omega\to\infty}\frac{1}{N_\Omega}\sum_L A_L(\kappa,E_n)\delta(E_{n'}(\kappa')-E_n(\kappa))\mathcal{A}_L(\kappa',E_{n'})=\begin{cases}\frac{1}{\tilde{\omega}}\delta_{nn'} & \text{for } \kappa=\kappa'\\ 0 & \text{otherwise},\end{cases} \tag{79}$$

which results in

$$\sum_L \left[\lim_{N_\Omega \to \infty} \frac{1}{N_\Omega} \sum_n A_{L'}(\kappa,E_n)\delta(E-E_n(\kappa))\mathcal{A}_L(\kappa,E_n) \right] A_L(\kappa,E_{n'}) = \begin{cases} \frac{1}{\tilde{\omega}} A_{L'}(\kappa,E_{n'}) & \text{if } E=E_{n'}(\kappa) \\ 0 \text{ otherwise} . \end{cases} \tag{80}$$

[Equations (77)–(80) represent the generalization of the corresponding relations for the case of a constant periodic potential[16] where these equations are easily derived from the translational properties of the Bessel functions.[20,27]] Then the function defined in Eqs. (56) and (59) becomes [compare with Eq. (62) and notice the same E dependence]

$$\tilde{\Phi}_L(\kappa,E^{1/2},\rho) = \lim_{N_\Omega \to \infty} \frac{1}{N_\Omega} \Phi_L(\kappa,E^{1/2},\rho) , \tag{81a}$$

$$\Phi_L(\kappa,E^{1/2},\rho) = \sum_n \Psi(\kappa,E_n,\rho)\tilde{\omega}\delta(E-E_n(\kappa))\mathcal{A}_L(\kappa,E_n) \tag{81b}$$

and has the property

$$\int_{\tilde{\Omega}} d\kappa e^{i\kappa\cdot\mathbf{R}} \Phi_L(\kappa,E^{1/2},\rho) = \tilde{\omega}\Phi_L(E^{1/2},\rho+\mathbf{R}) , \tag{82a}$$

$$\sum_L \tilde{\Phi}_L(\kappa,E^{1/2},\rho) A_L(\kappa,E_n) = \begin{cases} \Psi(\kappa,E_n,\rho) & \text{if } E=E_n(\kappa) \\ 0 \text{ otherwise} \end{cases} \tag{82b}$$

[compare with Eq. (64)]. Thus we have found the meaning of the folding procedure, Eq. (56), in the case of a general periodic potential: The regular solution, Eq. (12) with potential Eq. (29), at an arbitrary Bloch energy $E_{n'}(\kappa')$ when folded according to Eq. (56) for a fixed wave vector, say κ, will select, in the sense of Eq. (57), only the Bloch energies E_n. In other words, we have shown the existence of the Bloch-periodic orbitals $\tilde{\Phi}_L(\bar{\kappa},E^{1/2},\rho)$, Eq. (81b), which form an on-shell base, Eq. (82b), in the Hilbert space of Bloch functions defined by Eq. (31).

Equations (81) and (82) represent the main result of this paper. [Ultimately, it is Eq. (82b) which allows us to show that the band-structure equation derived in Ref. 16 represents an exact result, i.e., it generates the correct eigenvalues.] In fact, Eqs. (81) and (82) express the concrete (practical) relation between the Hamiltonian Eq. (65) (acting in the Hilbert space of square integrable functions) and the Bloch-periodic Hamiltonian (acting in the Hilbert space spanned by the plane waves $[(e^{i(\kappa+\mathbf{K})\cdot\rho}/\sqrt{\omega}]_\mathbf{K}$). In this sense, Eq. (81b) represents the extension of a result given in theorem XIII 98 in Reed and Simmon;[1] in the present notation, this result is written as

$$(E-E_n)\int_{\mathbb{R}^3} \Psi^*(\kappa,E_n,\mathbf{r})\Phi_L(E^{1/2},\mathbf{r})d\mathbf{r} = (E-E_n)\int_\Omega \Psi^*(\kappa,E_n,\rho)\Phi_L(\kappa,E^{1/2}\mathbf{r})d\mathbf{r}=0 \tag{82c}$$

So far, we have derived the existence of a new representation of the Bloch function as defined by Eq. (82b): Among various representations of the Bloch function as a superposition of Bloch-periodic orbitals, there is only one (by construction) which also has an on-shell character, although in a distribution sense. For completeness, we briefly compare this result with various related representations (complete details can be found in Ref. 16). By combining the representation given by Eq. (82b) with the multipole expansion Eq. (38) (which exists only for the inscribed sphere[22,23]) we are led to the representation[16]

$$\Psi(\kappa,E,\rho) = \begin{cases} \sum_L \Phi_L(E^{1/2},\rho)A_L(\kappa,E) & \text{for } \rho \le \mu \\ \sum_L \tilde{\Phi}_L(\kappa,E^{1/2},\rho)A_L(\kappa,E) & \\ \text{for } \rho\in\Omega,\ \rho\ge\mu , & \end{cases} \tag{82d}$$

which, at $E=E_n(\kappa)$, is to be compared with that given by Eq. (52). By retaining only the first term in the definition, Eqs. (57) and (59), of the (on-shell Bloch periodic) orbitals $\tilde{\Phi}_L(\kappa,E^{1/2},\rho)$ and introducing the corresponding Eq. (82b) into Eq. (34), one obtains a band-structure equation (derived by other means and claimed to be an exact result in Ref. 9) which represents a rather good approximation to the exact result.[9,13] Hence one might expect that by including the φ correction in Eq. (57), even for a small d, we may simulate the effect of many plane waves of Eq. (52). Finally, it needs to be emphasized that the existence of these on-shell Bloch-periodic orbitals was inferred solely from the eigenvalue equation, Eq. (31)—in a similar fashion to the case of a finite range potential, Eqs. (16)–(19)—and that no additional conjecture (such as is usually made concerning the completeness of the expansion functions) was invoked.

At this point one might ask for the difference, if any, between Eqs. (58) [or rather (82b)] and Eq. (50). As already mentioned at the end of Sec. III, a superposition of the regular solutions, $\Phi(E^{1/2},\rho)$, is not necessarily Bloch periodic, whereas a superposition of the orbitals defined by Eq. (81b) will automatically be Bloch periodic and, providing the coefficients are properly chosen, will give the Bloch function, Eq. (82b). More precisely, Eq. (58) or Eq. (82b) (in which each term is Bloch periodic) is a superposition in the Hilbert space $\mathcal{H}(\kappa)$ whereas Eq. (50) describes the multipole expansion of a function which coincides with the Bloch function *only* in a certain domain, namely, $r \le d$. In this sense, Eq. (50) contains less information than does either Eq. (58) or Eq. (32).

Actually, the Bloch function defined by Eq. (31) can be specified either (i) by giving the coefficients in Eq. (32) or (ii) by giving the coefficients *and* the regular solutions $\Phi_L^d(E^{1/2},\mathbf{r})$ in Eq. (49) in the limit $d=\infty$. In (ii), Eq. (50) corresponds only to a finite d, namely, the radius of

the circumscribing sphere. However, for the interior points of the unit cell, Eq. (50) can be approximately considered[16] as a superposition in the Hilbert space $\mathcal{H}(\kappa)$. To show this, we first recall the convergence property of the Fourier series:[1] assume the function $f(x)$, continuous in $[0,2\pi]$ and the corresponding Fourier coefficients

$$\hat{f}_n=\frac{1}{2\pi}\int_0^{2\pi}e^{-inx}f(x)dx \ . \tag{83a}$$

Then the Fourier series $\sum_n e^{inx}\hat{f}_n$ converges to $f(x)$ if $x\in(0,2\pi)$ and to $\frac{1}{2}[f(0)+f(2\pi)]$ at the endpoints. It follows that the function $\Phi_L^{\rm circ}(E^{1/2},\rho)$ corresponding to d, the radius of the circumscribing sphere, can be represented at any *interior* point of Ω as a series of the plane waves $(e^{i(\kappa+\mathbf{K})\cdot\rho})_{\mathbf{K}}$, whereas on the boundary of the unit cell this series converges to

$$\tfrac{1}{2}[\Phi_L^{\rm circ}(E^{1/2},\rho)+e^{i\kappa\cdot\mathbf{R}}\Phi_L^{\rm circ}(E^{1/2},\rho+\mathbf{R})] \ .$$

Thus in every domain included in the interior of the unit cell, Eq. (50) can be (approximately) handled as a superposition in the Hilbert space $\mathcal{H}(\kappa)$, i.e., as a superposition of Bloch-periodic terms.

Now that we have obtained more insight into the meaning of Eq. (50), we briefly examine (for completeness) the meaning of the superposition

$$f(E_n,\rho)=\sum_L \Phi_L^{\rm cell}(E_n,\rho)A_L(\kappa,E_n) \ , \tag{83b}$$

where $\Phi_L^{\rm cell}(E_n^{1/2},\mathbf{r})$ are the regular solutions, Eq. (12), of the cell potential $\mathcal{V}(\rho)$. Long ago,[6] such a superposition was believed to describe the Bloch function as an exact result; it is now considered as an approximation.[11]

It follows that Eq. (83b) coincides with Eq. (13) only for $\rho\le\mu$ and therefore, that it correctly describes the Bloch function only within the inscribed sphere. For $\rho\ge\mu$, however, the question is whether or not the sum in Eq. (83b) is convergent. In this respect, we notice that Eq. (50) was derived from Eq. (31), whereas Eq. (83b) was obtained by taking a particular prolongation of Eq. (38); also, Eq. (50) can be illustrated in a soluble case,[14] whereas there appears to be no particular case which shows the convergence of the sum in Eq. (83b). Suppose, however, that the sum in Eq. (83b) is convergent for $\rho\ge\mu$ (not only for $\rho\le\mu$), then the question arises as to its meaning. Clearly, such a superposition satisfies the Schrödinger equation for the cell potential $\mathcal{V}(\rho)$ (as a differential equation) but its being Bloch periodic [which has to be derived from Eqs. (34) and (37)] is very doubtful. Moreover, the representation of the Bloch function as given by the right-hand side of Eq. (83b) for $\rho\in\Omega$ but $\rho\ge\mu$ can neither be obtained from the eigenvalue equation, Eq. (31), nor from completeness considerations [because the Bloch functions and the regular solutions $\Phi_L^{\rm cell}(E^{1/2},\mathbf{r})$ belong to completely different Hilbert spaces[1]]. Finally, the soluble example of a constant periodic potential[16] shows that the representation given by Eqs. (49) and (50) is true whereas that given by Eq. (83b) is not. We conclude, therefore, that the right-hand side of Eq. (83b) can represent (approximately) the Bloch function at most in any interior domain of the unit cell Ω but definitely not at the boundary.

Concluding this section, we have shown that the multipole expansions, Eqs. (49) and (50), can be transformed into an on-shell superposition of Bloch-periodic orbitals. That is, we have shown the existence of a new base in the Hilbert space of Bloch-periodic functions which has an on-shell character. Based on this result, we show in the next section that the integral eigenvalue equation, Eq. (31), is equivalent (both necessary *and* sufficient) to a homogeneous system of linear equations for the A_L coefficients.

V. BAND-STRUCTURE EQUATION

As discussed at the end of the Sec. II, the band-structure equation can be obtained by collecting *all* the conditions satisfied by the $A_L(\bar{\kappa},E_n)$. In this respect, the homogeneous system obtained by introducing Eq. (50b) into Eq. (34) represents only a necessary condition; for sufficiency it has to be supplemented with the homogeneous system obtained by introducing Eq. (56) into Eq. (40).[32]

Now the point is that we can keep track of the conditions given by Eq. (40) by simply using in Eq. (34) the superposition defined by Eq. (58) where each term belongs to the space $\mathcal{H}(\kappa)$ in the sense of Eq. (56).[33] Actually, assume, for a fixed wave vector κ and an arbitrary Bloch energy E (not necessarily at the point κ), the following homogeneous linear system

$$\sum_{L'}\mathcal{C}_{LL'}(\kappa,E)A_{L'}=0 \ , \tag{84}$$

where both E and $A_L(\kappa)$ are unknown and the matrix $\mathcal{C}(\kappa,E)$ is defined by

$$\mathcal{C}_{LL'}(\kappa,E)=\delta_{LL'}-\frac{\pi E^{1/2}}{2}\int_\Omega n_L^*(\kappa,E^{1/2},\rho)\mathcal{V}(\rho)\times\Phi_{L'}(\kappa,E^{1/2},\rho)d\rho \ , \tag{85}$$

which, by using Eqs. (56) and (34), becomes

$$\mathcal{C}_{LL'}(\kappa,E)=\delta_{LL'}-\lim_{N_\Omega\to\infty}\frac{\tilde{\omega}}{N_\Omega}\times\sum_n A_L(\kappa,E_n)\delta(E-E_n(\kappa))\mathcal{A}_{L'}(\kappa,E) \ . \tag{86}$$

By now using Eq. (80) we conclude that Eq. (84) has a nonzero solution if and only if E happens to be a Bloch energy at the point κ [i.e., $E=E_n(\kappa)$] and the corresponding solution is represented by the $A_L(\kappa,E_n)$ as defined in Eqs. (33) and (34).[34] Thus we have found that the eigenvalue problem, Eq. (31), in the space $\mathcal{H}(\kappa)$ is equivalent to an algebraic homogeneous linear system, Eq. (84), similar to the simple case of a finite-range potential, Eqs. (14) and (20), respectively. This finding represents the main result of the present paper. [The soluble case of a constant periodic potential can be found in Ref. 16 where Eq. (84) was derived as a neces-

sary condition only, but revealed itself to be also a sufficient condition.] Equation (84) provides a solution to the problem of the periodic potential by using the L representation and a limiting procedure: For successive values of $d \to \infty$, the system

$$\sum_{L'} \mathcal{C}^d_{LL'}(\kappa,E) A_{L'} = 0 , \tag{87}$$

where the matrix $\mathcal{C}^d(\kappa,E^{1/2})$ is defined by

$$\mathcal{C}^d_{LL'}(\kappa,E) = \delta_{LL'} - \frac{\pi E^{1/2}}{2} \int_\Omega n^*_L(\kappa,E^{1/2},\rho) \mathcal{V}(\rho) \times \Phi^d_{L'}(\kappa,E^{1/2},\rho) d\rho \tag{88}$$

offers a systematic approximation to the Bloch function, Eq. (31), and in the limit $d = \infty$ yields the exact result. In particular, the eigenvalues are solutions of

$$\det \mathcal{C}(\kappa,E) = 0 \tag{89}$$

and, therefore can be approximated by the solutions of

$$\det \mathcal{C}^d(\kappa,E) = 0 . \tag{90}$$

The main advantage of Eq. (84) or (87), (which, in fact, motivated the present analysis) is represented by the fact that the effect of the structure was partially separated by means of the Bloch-periodic Neumann function $n_L(\kappa,E^{1/2},\rho)$ which, in the case of close-packed lattices, can be further written in terms of the usual structure constant, Eq. (36). This feature comes from Eq. (34) which suggested the use of an on-shell representation for the Bloch function; along this line, it is advantageous to use Eq. (57) to write

$$\mathcal{C}(\kappa,E) = \mathcal{C}^{\rm circ}(\kappa,E) + \lim_{d\to\infty} \Delta^d(\kappa,E) ,$$

$$\Delta^d_{LL'}(\kappa,E) = -\frac{\pi E^{1/2}}{e} \int_\Omega n^*_L(\kappa,E^{1/2},\rho) \mathcal{V}(\rho) \times \varphi^d_{L'}(\kappa,E^{1/2},\rho) d\rho \tag{91}$$

where the matrix $\mathcal{C}^{\rm circ}(\kappa,E)$ corresponds to the regular solution of the potential enclosed by the circumscribing sphere

$$\mathcal{C}^{\rm circ}(\kappa,E) = \Gamma^{\rm circ}(E) - \mathfrak{C}^{\rm circ}(\kappa,E) ,$$

$$\Gamma^{\rm circ}_{LL'}(E) = \delta_{LL'} - \frac{\pi E^{1/2}}{2} \int_\Omega n^*_L(E,\rho) \mathcal{V}(\rho) \times \Phi^{\rm circ}_{L'}(E,\rho) d\rho , \tag{92}$$

$$\mathfrak{C}^{\rm circ}_{LL'}(\kappa,E) = \frac{\pi E^{1/2}}{2} \int_\Omega n^*_L(\kappa,E,\rho) \mathcal{V}(\rho) \Phi^{\rm circ}_{L'}(E,\rho) d\rho .$$

Now in the case of close-packed lattices, we have [from Eq. (36)]

$$\mathcal{C}^{\rm circ}(\kappa,E) = \Gamma^{\rm circ}(E) - \mathbf{N}(\kappa,E) \Sigma^{\rm circ}(E) , \tag{93a}$$

where

$$\Sigma^{\rm circ}_{LL'}(E) = \frac{\pi E^{1/2}}{2} \int_\Omega j^*_L(E,\rho) \mathcal{V}(\rho) \Phi^{\rm circ}_{L'}(E,\rho) d\rho , \tag{93b}$$

and the matrix $\mathbf{N}(\kappa,E)$ represents the usual structure constants.[3,4] As we can see, the effects of structure in Eq. (92) are decoupled from those of the potential; even more, the structure in Eq. (93) is described by means of the usual structure constants, as in the KKR equation. Thus, if we neglect the second term in Eq. (91) and confine ourselves to the case of close-packed lattices, we obtain the result derived and claimed as exact in Ref. 9: the structure is not only separated but is also described by the usual structure constants. It is clearly that the exact result, Eq. (91), differs from that of Ref. 9 by the presence of corrections Δ which reflect the Bloch periodicity described within the multipole expansion. It follows that the result of Ref. 9 [obtained here by simply introducing Eq. (50b) into Eq. (34)] corresponds to an approximation which breaks the Bloch periodicity in the sense that the Bloch function in Eq. (34) is not represented as a superposition in the space $\mathcal{H}(\kappa)$. However, in view of the convergence properties of the Fourier series discussed at the end of Sec. IV, Eq. (50b) can be considered as an approximate superposition in $\mathcal{H}(\kappa)$ but only at the interior points of the unit cell. Since the Bloch function in this approximation satisfies the Schrödinger equation only as a differential equation (i.e., without Bloch-periodic boundary conditions) it can also be represented as given by Eq. (83b). By introducing Eq. (83b) into Eq. (34) and again restricting oneself to the case of close-packed lattices, we obtain a band-structure equation which was first derived and claimed as an exact result in Ref. 6. Subsequently, this equation was shown (by using either theoretical considerations,[7–9,11,12,14,15] or by computational means[13] or by studying a soluble example[16]) to represent only an approximate result. Recently, however, Ref. 10 claims to have proven that such an equation represents an exact result. In Ref. 16, we showed that the results presented in Refs. 9 and 10 as exact results correspond, in fact, to the same approximation which we call the "generalized muffin-tin approximation."

Alternatively, the relation between structure and potential in Eq. (91) can be studied by isolating, with the help of Eq. (82d), the muffin-tin contribution

$$\mathcal{C}(\kappa,E) = \mathcal{C}^{\rm MT}(\kappa,E) - \lim_{d\to\infty} \frac{\pi E^{1/2}}{2} \int_{\Omega\setminus S^{\rm MT}} n^*_L(\kappa,E,\rho) \mathcal{V}(\rho) \times \tilde{\Phi}^d_{L'}(\kappa,E,\rho) d\rho ,$$

$$\mathcal{C}^{\rm MT}(\kappa,E) = \Gamma^{\rm MT}(\kappa,E) - \mathbf{N}(\kappa,E) \Sigma^{\rm MT}(\kappa,E) \tag{94}$$

where the matrices are obtained from Eqs. (92) and (93b) by replacing the function $\Phi^{\rm circ}$ with the function $\Phi^{\rm MT}$. Now compare Eq. (94) with Eq. (53a); since in Eq. (52b) each term alone does not satisfy the Schrödinger equation, we have to consider in Eq. (53a) many plane waves. By contrast, Eq. (58) represents an on-shell superposition which, by retaining only the first term in Eq. (57a), coincides with an approximate result[9] that was already seen to yield good accuracy.[9,13] It then appears plausible that including the second term in Eq. (94) [or considering the

Δ correction in Eq. (91)] will be equivalent to the inclusion of many plane waves in Eq. (53a).

Equations (84)–(91) were first derived in Ref. 16 where they reflected only a necessary condition which, however, happens to also be sufficient in the soluble case of constant periodic potential. [In fact, the sufficiency proof contained in Eqs. (54)–(86) was inspired by this case.] Reference 16 also contains a detailed discussion of the Δ corrections (called, after their effect, "multipole expansion periodicity corrections") including the illustration of their role in a soluble case as well as the circumstances in which these corrections might be disregarded (the generalized muffin-tin approximation).

Finally, the striking resemblance of Eq. (85) with the corresponding equation for a finite-range potential, Eq. (22b), raises the question as to the possible meaning of the Σ and Γ matrices in the sense of (generalized) phase shifts depending not only on E but also on κ. In fact, such a meaning is brought about by a study of the T operator corresponding to a general periodic potential[35] and, perhaps more relevant, by finding a Friedel-type sum rule for a general periodic potential.[36]

VI. SUMMARY AND CONCLUSIONS

We have developed a method to solve the boundary condition problem of a differential equation by expressing the corresponding solution as a superposition of the independent solutions of this differential equation (in a Wronskian sense). The coefficients of this superposition are determined from an algebraic linear system which expresses the boundary conditions. (Note that in a diagonalization procedure the boundary conditions are always satisfied and the corresponding linear system expressed the solution of the differential equation.) Hence the main virtue of our procedure consists of treating on an equal footing various boundary conditions, in particular Bloch-periodic boundary conditions and those for a Hamiltonian with finite-range potential. However, while the implementation of this method is almost trivial in the case of a finite-range potential, the case of a periodic potential raises the problem of describing the Bloch periodicity by using multipole expansions. Thus we first described the (Bloch periodic) prolongation of the Bloch function in an arbitrary sphere as a multipole expansion and, subsequently, by using a folding procedure, we found the Bloch function as an on-shell superposition of Bloch-periodic orbitals. The crucial point in obtaining this representation was expressed by Eqs. (81) and (82), which established the existence of a new base in the space of Bloch-periodic functions. By using these equations, we demonstrated the equivalence between the integral eigenvalue equation of the Bloch function and an algebraic homogeneous linear system of equations (first introduced in Ref. 16) for the coefficients of the multipole expansion of the Bloch function at the origin. In contrast to the KKR equation, this system exhibits a supplementary structure dependence which does not allow for the structure to be separated from the potential. However, this supplementary structure dependence can be isolated in the form of a correction (multipole expansion periodicity correction[16]) which, ultimately, assures the equivalence mentioned above (an example was previously considered for the soluble case of a constant periodic potential.)[16] Finally, the band-structure equation derived here (for a general periodic potential) coincides with the equation of the poles of the on-shell T matrix recently determined in Ref. 35 by establishing (and using) a direct integral decomposition of the T operator for a general periodic potential.

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[4]W. Kohn and N. Rostoker, Phys. Rev. **94**, 1111 (1954).

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[13]J. S. Faulkner [Phys. Rev. B **32**, 1339 (1985); **34**, 5931 (1986)] presents a pertinent account on the present "state of the art" of separability between structure and potential and also gives a list of relevant references. In particular, he proves in the second paper, by means of a clearly convergent computation, that the "near-field corrections," although small, are different from zero in the special case of a constant potential and two-dimensional square lattice. Obviously, in the case of deformed unit cells, these corrections are expected to become more important.

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

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

[17]F. Calogero, *Variable Phase Approach to Potential Scattering* (Academic, New York, 1967); J. R. Cox, Nuovo Cimento **37**, 474 (1965); C. Zemach, *ibid.* **33**, 939 (1964). Some particular aspects of this method, when applied in solid-state physics

where the potential is essentially nonspherical, can be found in Ref. 8. Recent applications in (muffin-tin) computations are reported in D. D. Johnson, F. J. Pinski, and G. M. Stocks, Phys. Rev. B **30**, 5508 (1984). Recently, more efficient computational versions can be found in C. Dullemond, D. Gupta, T. A. Rijken, and E. van Beveren, Comp. Phys. Commun. **27**, 377 (1982); and V. Rokhlin, J. Comp. Phys. **60**, 187 (1985).

[18]As usual, the potential is allowed to be singular at the origin at most as $1/\rho^{2-\epsilon}$, $\epsilon \geq 0$. In view of using the variable-phase method, i.e., Eqs. (12c) and (13c), to compute the functions defined in Eqs. (12a)–(13b) we need the supplementary condition that the potential is spherically symmetric at the origin, that is $V^d_{LL'}(\rho) \to \delta_{LL'}/\rho^{2-\epsilon}$ as $\rho \to 0$. (This condition is required by the behavior of Bessel and Neumann functions at the origin.) In order to compute the solutions of Eqs. (12c) and (13c) for potential Eq. (29) we should make a cutoff near the origin, and, obviously, the larger d is, the higher L should be, which is not convenient for practical computation. However, as will be seen later, it is not necessary to consider large d in practice. Without introducing this cutoff, the potential is singular at the origin, and hence at any lattice vector $\mathbf{r}=\mathbf{R}$; Eqs. (12a)–(13b) still have solutions which, however, can no longer be computed with Eqs. (12c) and (13c) across the spheres having radius **R**. In this case, (as well as in the case of many atoms per unit cell) the solution should be computed around each unit cell center and afterwards matched on an intermediary sphere or, alternatively, along the computational lines introduced in Ref. 14.

[19]We discuss here only the case of positive energy. For $E<0$, we should replace the kernel of the (Bloch periodic) Green function in Eqs. (14) and (31) according to $\cos E^{1/2}r \to e^{-(-E)^{1/2}r}$. This results in everywhere changing $E^{1/2} \to i(-E)^{1/2}$ and $n_L \to j_L + i n_L$.

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[22]The Bloch function obeys an ordinary Schrödinger equation with potential V^μ inside the inscribed sphere. In this domain the Laplacian can be separated in spherical coordinates and the orthogonality of spherical functions can be used to obtain a coupled channel equation for multipole moments which finally results in Eq. (38). See also Ref. 23 below.

[23]The philosophy behind the introduction of the function $\Psi^d(\boldsymbol{\kappa},E_n,\mathbf{r})$ can be summarized as follows: A function $f^\Omega(\boldsymbol{\rho})$ defined on a nonspherical domain Ω does not have a multipole expansion, for we can calculate the integrals $f^\Omega_L(\rho)=\int_{4\pi} Y^*_L(\hat{\rho}) f^\Omega(\boldsymbol{\rho}) d\hat{\rho}$ 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

$$f^\Omega(\boldsymbol{\rho})=\sum_L Y_L(\hat{\mathbf{r}}) f^S_L(r)\Big|_{\mathbf{r}=\boldsymbol{\rho}\in\Omega} .$$

However, this is not a multipole expansion of $f^\Omega(\boldsymbol{\rho})$, for, in particular, it is nonunique. We choose, in the text, a Bloch-periodic prolongation only because its equation can be easily obtained from Eq. (31). Note that in contrast to the Bloch function $\Psi(\bar{\kappa},E_n,\boldsymbol{\rho})$, the functions $\Phi^\mu_L(E^{1/2},\boldsymbol{\rho})$ exist for any energy; hence the notation. We omit the $\boldsymbol{\kappa}$ dependence of E in $\Psi(\boldsymbol{\kappa},E_n,\boldsymbol{\rho})$ and $A_L(\bar{\kappa},E_n)$, but keep this dependence in $\Phi^\mu_L(E_n^{1/2}(\boldsymbol{\kappa}),\boldsymbol{\rho})$, $j_L(E_n^{1/2}(\boldsymbol{\kappa}),\boldsymbol{\rho})$, $n_L(\boldsymbol{\kappa},E_n^{1/2}(\boldsymbol{\kappa}),\boldsymbol{\rho})$, and, later on, in every function which, in contrast to the Bloch function, contains the energy E and $\boldsymbol{\kappa}$ as independent variables.

[24]Because their expansion [as elements of $L^2(\mathbb{R}^3)$, cf. Eq. (25) and theorem XII 98 in Reed and Simmon[1]] in terms of the Bloch functions, Eq. (66), contains all the wave vectors $\boldsymbol{\kappa}\in\tilde{\Omega}$. A more detailed analysis of the regular solution follows in Sec. IV.

[25]The matrix elements $V^d_{LL'}(r)$ have selection rules given by the crystal symmetry, which reduces the dimension of the L space. Alternatively, one can work from the beginning with superpositions of spherical functions having the lattice symmetry.

[26]The representation, Eq. (50), was previously addressed[8,9] but only for d, the radius of the circumscribing sphere, and without introducing the coefficients $A_L(\boldsymbol{\kappa},E)$ as derived in Eqs. (33) and (34).

[27]In the case of a constant potential, the function $\Phi_L(E^{1/2},\mathbf{r})$, $E\geq 0$, still remains an element of $L^2(\mathbb{R}^3)$ in the sense of

$$\int_{\mathbb{R}^3} j^*_L(E^{1/2},\mathbf{r}) j_L(E^{1/2},\mathbf{r}) E d\mathbf{r} = \delta_{LL'}\delta(E^{1/2}-E'^{1/2}) ,$$

which guarantees the existence of the Fourier transform

$$j_L(E^{1/2},\mathbf{r})=\int_{\mathbb{R}^3}\frac{e^{i\mathbf{p}\cdot\mathbf{r}}}{(2\pi)^{3/2}}\frac{\delta(p-E^{1/2})}{p^2} i^{-l} Y_L(\hat{p}) d\mathbf{p}$$

and

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

which, in turn, makes the limits Eqs. (58) and (59) obvious. This type of property is not apparent in the general case of an arbitrary potential. Then, in order to still get some illustrative information, we avoided[16] the use of the above normalization and confined ourselves only to the use of translational properties of the Bessel functions.[20] Later on, the treatment of the general potential will consist of finding a relation which expresses $\Phi_L(E^{1/2},\mathbf{r})$ in terms of $\Psi(\boldsymbol{\kappa},E_n,\mathbf{r})$ which, in fact, generalizes the above Fourier transform, and hence makes the translational properties of $\Phi_L(E^{1/2},\mathbf{r})$ obvious.

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

[29]In fact, Eqs. (64) represent a complementary point of view to that illustrated by Eqs. (58). Actually, Eqs. (58) [derived from the eigenvalue equation (31)] gives the Bloch function as an on-shell superposition of periodic orbitals defined in Eq. (59), whereas Eq. (64) says that the periodic orbitals defined in Eq. (62) [and derived from Eq. (12) and from the translational properties of Bessel functions (36)] exist as an on-shell base in the space of Bloch functions.

[30]One might say that Eq. (22a) with potential Eq. (29) has no solutions for a positive potential because a particle at a positive energy will be able to tunnel any (finite) wall and eventually reach infinity. [That is, the Hamiltonian, Eq. (65), has no bound states for a positive potential.] However, according to Eastham and Kalf (Ref. 2) "this guess is wrong because it does not take account of the possibility that a succession of well arranged bumps at sufficient height might create a standing wave pattern and thus trap the particle." The first such example was given by von Neumann and Wigner (in 1929) and an extensive discussion of this point can be found in Eastham and Kalf (Ref. 2).

[31]This result can be easily checked in the case of a constant po-

tential, where the regular solution is known and its Fourier transform was given in Ref. 27. Details concerning the definition of the δ function as solution of the (functional) equation $x\delta(x)=0$ can be found, e.g., in J. Schwinger, *Quamtum Kinematics and Dynamics* (Benjamin, New York, 1970).

[32]An approximate (and perhaps computationally convenient) result can be obtained by adding to the equation obtained by introducing Eq. (50b) into Eqs. (34) the system of equations obtained by considering Eqs. (50b) and (40a) on a grid on the surface of the unit cell.

[33]Because the Bloch function, as an element of the Hilbert space $\mathcal{H}(\kappa)$, is described by Eq. (58) and not by Eq. (50).

[34]Essentially, this result was obtained by using Eq. (80). Alternatively (in a more formal way), one can say that Eq. (34) expresses a property which holds in the Hilbert space of Bloch-periodic functions. Then the use of representation Eq. (58) or (82b) in Eq. (34) becomes mandatory. Yet we do not know whether Eq. (84) gives the same band structure as that given by the plane-wave diagonalization or has other roots as well; hence the need for the proof contained in Eqs. (85) and (86), which relies on the results derived in Sec. IV.

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