

Rigorous (nonvariational) solution of the Schrödinger equation for a crystal

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A formalism is developed for a rigorous (nonvariational) solution of the single-particle Schrödinger equation for a many-atom system described by a potential of arbitrary form. The method can be used for arbitrary crystals with chemical bonds of various types. For "muffin-tin" potentials the equations of the method reduce to the known equations of the Korringa–Kohn–Rostoker theory. The correctness of the method is verified by a numerical analysis of the three-dimensional periodical Mathieu potential for which exact analytic solutions are known.

1. FORMULATION OF PROBLEM

The theory of the electronic structure of crystals is based on the single-particle Schrödinger equation (SE)

$$[-\nabla^2 + V(\mathbf{r}) - E]\psi(\mathbf{r}) = 0. \quad (1)$$

The effective potential $V(\mathbf{r})$ is invariant to displacements of the coordinate frame along arbitrary lattice translation vectors \mathbf{r}_n :

$$V(\mathbf{r} + \mathbf{R}_n) = V(\mathbf{r}).$$

The solutions $\psi(\mathbf{r})$ should satisfy the Bloch theorem

$$\psi_{\mathbf{k}}(\mathbf{r} + \mathbf{R}_n) = \exp(ik\mathbf{R}_n)\psi_{\mathbf{k}}(\mathbf{r}). \quad (2)$$

They are therefore classified by a wave vector \mathbf{k} located in the first Brillouin zone.

A number of methods, forming jointly the band theory, have been proposed for the solution of the boundary-value problem (1), (2). It is appropriate to gather these methods into two groups: variational methods [pseudopotential, orthogonalized plane waves (OPW), linear combinations of atomic orbitals (LCAO), linear combinations of "muffin-tin" orbitals (LMTO) and "joining" methods [cell method, augmented plane waves (APW), Korringa–Kohn–Rostoker (KKR) Green's functions].¹ The variational methods are based on representation of the sought function $\psi_{\mathbf{k}}$ by an expansion

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_i a_{i\mathbf{k}} \varphi_{i\mathbf{k}}(\mathbf{r})$$

in some set of basis functions $\varphi_{i\mathbf{k}}$ that satisfy boundary conditions (the Bloch theorem). The boundary-value problem (1), (2) is replaced by a variational problem of finding the extrema of an energy functional with respect to variation of the coefficients $a_{i\mathbf{k}}$. The choice of the form of the basis functions (plane waves, orthogonalized plane waves, atomic orbitals) determines the corresponding method (pseudopotential, APW, LCAO). It is important that the basis functions $\varphi_{i\mathbf{k}}$ are not solutions of the initial SE (1). As a result, given a certain potential $V(\mathbf{r})$, different methods lead to different solutions that do not tend to the solution of the initial problem as the number of basis function is increased. Depending on the type of the chemical bond in the crystal (simple metals, transition metals, covalent semiconductors, transition-metal oxides, etc.), one method or another is chosen by starting from the physical requirement of a reasonable

approximation of the sought function $\psi_{\mathbf{k}}$ by one set of functions or another.

Each of the variational methods has thus a limited applicability and yields, from the fundamental point of view, an approximate solution of the initial problem.

The joining methods are based on the requirement that the function $\psi_{\mathbf{k}}$ be continuous together with its first derivatives everywhere in the crystal. A rigorous formulation of these methods is possible only for a limited class of potentials of the so-called "muffin-tin" (MT) form. The crystalline MT potential is represented by a superposition

$$V^{\text{MT}}(\mathbf{r}) = \sum_n u_n(\mathbf{r} - \mathbf{R}_n) \quad (3)$$

of "atomic" MT potentials

$$u_n(\mathbf{r}_n) \equiv u_n(\mathbf{r} - \mathbf{R}_n) = \begin{cases} u_n(|\mathbf{r}_n|), & |\mathbf{r}_n| \leq b_n, \\ 0, & |\mathbf{r}_n| > b_n, \end{cases} \quad (4)$$

each of which differs from zero only within "its own" MT sphere having a radius b_n .

Our aim here is to develop a method that leads to a rigorous (nonvariational) solution of the problem (1), (2) for an effective crystal potential of arbitrary form. The method should be valid for crystals with various types of chemical bond.

The need for restricting ourselves to the class of MT potentials in the traditional formulation, and a criticism of the concept of multiple scattering, are analyzed in Sec. 2. The general formalism is considered in Sec. 3. A particular case of an MT potential is analyzed in Sec. 4. The correctness of the method is verified by a numerical analysis of a three-dimensional periodic Mathieu potential, for which an exact analytic solution is known. The results of a numerical analysis are given in Sec. 5. The distinctive features of the Green's function of a system of many centers are considered in the Appendix.

2. JOINING OF WAVE FUNCTIONS IN THE CONTEXT OF THE MULTIPLE SCATTERING CONCEPT

An analysis of an attempt to obtain a rigorous solution by joining wave functions is best carried out by using the multiple-scattering concept. We transform from the boundary-value problem (1), (2) to the integral SE

$$\psi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{N} \int G_{\mathbf{k}}(\mathbf{r}, \mathbf{r}'; E) V(\mathbf{r}') \psi_{\mathbf{k}}(\mathbf{r}') d^3r'. \quad (5)$$

The integration here is over the main region of the crystal, containing N unit cells of volume Ω . The Green's function (GF) satisfying the periodic boundary conditions is expressed by a series in the reciprocal-lattice vectors \mathbf{k}_μ :

$$G_{\mathbf{k}}(\mathbf{r}, \mathbf{r}'; E) = -\frac{1}{\Omega} \sum_{\mathbf{k}_\mu} \frac{\exp[i(\mathbf{k} + \mathbf{K}_\mu)(\mathbf{r} - \mathbf{r}')] }{|\mathbf{k} + \mathbf{K}_\mu|^2 - E}. \quad (6)$$

On the basis of the multiple-scattering idea, we represent the crystal potential V as a superposition of the potentials v_n of the individual cells:

$$V(\mathbf{r}) = \sum_n v_n(\mathbf{r} - \mathbf{R}_n) = \sum_n v_n(\mathbf{r}_n),$$

$$v_n(\mathbf{r} - \mathbf{R}_n) = \begin{cases} v_n(\mathbf{r}_n), & \mathbf{r} \in \Omega_n, \\ 0, & \mathbf{r} \notin \Omega_n. \end{cases} \quad (7)$$

Equation (5) is then equivalent to the system

$$\psi_{\mathbf{k}}(\mathbf{r}_m) = \frac{1}{N} \sum_{n=1}^N \int_{\Omega_n} G_{\mathbf{k}}(\mathbf{r}_m, \mathbf{r}_n' + \mathbf{R}_{mn}; E) v_n(\mathbf{r}_n') \psi_{\mathbf{k}}(\mathbf{r}_n') d^3\mathbf{r}_n',$$

$$\mathbf{R}_{mn} = \mathbf{R}_n - \mathbf{R}_m, \quad m = 1, 2, \dots, N. \quad (8)$$

We shall assume that each of the potentials v_n vanishes in a thin layer of thickness δ in the vicinity of the faces of the cell n . (The quantity δ must tend to zero in the final expressions.) Then, placing the point \mathbf{r}_m in a small δ -vicinity of the surface of cell m , we can use in the left-hand sides of Eqs. (8) the form of the solution $\psi_{\mathbf{k}}$ known for a zero potential. On the other hand, the functions $\psi_{\mathbf{k}}$ for all $\mathbf{r}_n' \in \Omega_n$ can be expanded in some complete system of functions χ_{nE} that are solutions of an SE with potential v_n at a certain energy E :

$$\psi_{\mathbf{k}}(\mathbf{r}_n') = \sum_n A_n \chi_{nE}(\mathbf{r}_n'), \quad \mathbf{r}_n' \in \Omega_n.$$

A proof of this statement is given in Ref. 2. By considering in succession the δ -vicinities of all the cells ($m = 1, 2, \dots, N$), we reduce the system of integral equations (8) to an algebraic system for the unknown coefficients A_n .

From the physical viewpoint this approach corresponds to the Rayleigh-Huygens self-consistency condition for diffraction of a wave by a many-center object. On the one hand, the wave field in a small δ -vicinity of each of the cells m should be determined by the asymptotic behavior of a wave scattered by the potential v_m . On the other hand, this very same field should be a superposition of the fields scattered by all cells. The self-consistency condition consists of equating (in the δ -vicinity of each cell) the amplitudes of the wave scattered by the given cell to the amplitude of the superposition of the waves scattered by all the cell.

The above concept of multiple scattering for a potential V of arbitrary shape, proposed in Refs. 3 and 4, does not solve, however, our problem. It is clear from the form of the system (8) that to make it algebraic it is necessary to be able, at a definite stage, to eliminate the explicit dependence on the actual position of the point \mathbf{r}_m . This requires that the right-hand side of (8) have a fully defined functional form of a dependence on \mathbf{r}_m . At the same time, the properties of the "atomic" potentials v_n dictate a transition to the concept of an angular momentum $|L\rangle = |lm\rangle$. It is obvious in this case that the possibility of obtaining an algebraic system is gov-

erned by the existence of a single-valued two-center (with respect to the centers m and n) expansion of the GF (6) in the spherical harmonics Y_L .

It turns out that the functional form of such an expansion depends on the relations between the quantities r_m, r_n' and R_{mn} , that enter in the arguments of the GF in (8) (see the Appendix). Let us consider neighboring cells m and n and place the point \mathbf{r}_m in a δ -vicinity of the surface of the cell Ω_m . In the calculation of the right-hand sides of (8) the point \mathbf{r}_n' runs through the entire volume of the cell n , and in some part of the volume of the cell Ω_n we have the inequality

$$r_m + r_n' < R_{mn}, \quad (9)$$

in some other part we have the inequality

$$r_m + R_{mn} < r_n' \quad (10)$$

and in other regions of the cell n are possible in principle other relations between r_m, r_n' and R_{mn} . (The forms of the inequalities and the shapes of the corresponding regions depend on the crystal geometry.) This means that for each such region inside the cell n it is necessary to use a specific two-center expansion of the GF—either (A6), or (A9), or some other (see the Appendix). Moreover, the choice of any of the GF expansion depends on the position of the point \mathbf{r}_m . The absence of a single two-center expansion for the GF makes it impossible to determine uniquely the functional form of the dependence of the field superposition (8) on the position of the point \mathbf{r}_m in the vicinity of the surface of the cell m . Consequently, to calculate the contributions from neighboring cells in (8), called the near-field contributions,⁴ it is necessary to evaluate the integrals in (8) with the total GF (6) independently for each actual position of the point \mathbf{r}_m . The presence of near-field contributions makes it impossible therefore to reduce the problem to algebraic within the framework of the multiple-scattering concept, making a numerical analysis practically impossible.

Changing to MT potentials (3) and (4) results in a substantial simplification. The integration region in each term of the right-hand side of (8) is bounded by a sphere Ω_n^{MT} inscribed in the cell n , since the potential outside the sphere is zero by definition. We introduce a thin layer of thickness δ on the inner side of the Ω_n^{MT} sphere and place the point \mathbf{r}_n in this layer. One and the same inequality (9) is then satisfied for arbitrary m and n and for any position of the point \mathbf{r}_m in this spherical layer. We can therefore use a unique expansion of the GF (A6), and this determines fully the functional form of the superposition of the fields (8) in the vicinity of the surface of the MT sphere Ω_n^{MT} . This allows the system (8) to be reduced to algebraic and yields the known equation of the KKR method of the band theory¹ (see Sec. 3).

It follows from this analysis that the near-field effects should make a solution of our problem impossible. Nonetheless, many attempts were made to develop a formalism on the basis of the multiple-scattering concept. A characteristic feature of these theories is that the secular equation contains t -matrix elements, or generalized phase shifts, which describe scattering of an isolated unit cell n by the potential v_n (7). A bibliography of these approaches can be found in Ref. 5. We note in addition that the frequently used model of overlapping MT spheres is also incorrect.

3. GENERAL FORMALISM FOR A CRYSTAL POTENTIAL OF ARBITRARY FORM

The key to the solution of the problem is to forgo the multiple-scattering concept in its traditional formulation. That is to say, forgo a representation of the potential in the form (7) and the attempt of determining the fields in the vicinities of the cell surfaces, i.e., in a region asymptotic to the atomic potentials v_n . We stipulate instead satisfaction of the Rayleigh-Huygens self-consistency condition at an arbitrary point \mathbf{r}_m located inside a certain sphere D_m having a radius smaller than the difference of the distance R_{mn} to the nearest cell n and than the radius of the sphere O_n drawn around the cell n (see Fig. 1). It is obvious then that the inequality (9) will be satisfied for all cell pairs m and n and for all $\mathbf{r}_m \in D_m$. This means that we can use the single-valued expansion (A6) of the GF. In other words, the functional form of the dependence of the superposition (8) is completely defined inside the sphere D_m .

The derivation given below was obtained for a particular case of a single-atom crystal. Generalization to the case of a many-atom crystal is trivial. We note only that it is always possible to break up the crystal space into polyhedra that ensure satisfaction of the inequality (8) inside spheres D_m . These polyhedra need not necessarily be unit cells in the crystallographic sense, and no atomic positions need be associated with some of them.

With the aid of the Bloch theorem, we reduce the integration over the principal region in (8) to integration over the unit cell Ω :

$$\psi_{\mathbf{k}}(\mathbf{r}) = \int_{\Omega} G_{\mathbf{k}}(\mathbf{r}, \mathbf{r}'; E) v(\mathbf{r}') \psi_{\mathbf{k}}(\mathbf{r}') d^3r', \quad \mathbf{r} \in D.$$

Using Green's theorem, we change to integration over a surface

$$\oint_{\sigma} d\sigma' [G_{\mathbf{k}}(\mathbf{r}, \mathbf{r}'; E) \nabla' \psi_{\mathbf{k}}(\mathbf{r}') - \psi_{\mathbf{k}}(\mathbf{r}') \nabla' G_{\mathbf{k}}(\mathbf{r}, \mathbf{r}'; E)] = 0, \quad \mathbf{r} \in D. \quad (11)$$

Here $d\sigma$ is the differential element of an area oriented along the outward normal to the cell surface.

We define a certain set of functions χ_L satisfying, inside the sphere O circumscribing the sphere, the SE (1) with a total potential:

$$[-\nabla^2 + V(\mathbf{r}) - E] \chi_L(E, \mathbf{r}) = 0, \quad \mathbf{r} \in O. \quad (12)$$

It is important that we seek regular solutions χ_L specified by boundary conditions at zero, and impose no requirements on

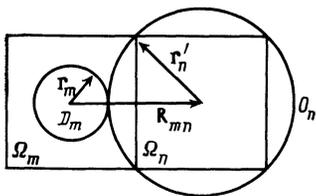


FIG. 1. Schematic representation of two neighboring unit cells Ω_m and Ω_n with the distance between centers equal to the lattice vector \mathbf{R}_{mn} . The sphere O_n circumscribes the cell n , and the sphere D_m is tangent to the sphere O_n . The radius vector \mathbf{r}_m occupies arbitrary positions in D_m , while \mathbf{r}'_n runs through the entire cell Ω_n .

the asymptotic behavior of these functions. In other words, we forgo the representation of the total potential V as a superposition (7) of atomic potentials each of which vanishes outside its own cell. The boundary conditions on the cell surface will be satisfied only for the total function $\psi_{\mathbf{k}}$ obtained by solving Eq. (11), simultaneously with finding the energy eigenvalue. The classification of the solutions χ_L by values of the angular momentum L is determined by the behavior of the solutions as $r \rightarrow 0$, inasmuch as in a small vicinity of zero the potential $V(\mathbf{r})$ can be regarded as spherically symmetric. It is just this feature of the behavior of the crystal potential near atomic nuclei which makes advantageous, as mentioned in Sec. 2, the transition to the angular-momentum representation.

Let us obtain equations for χ_L . The potential V and the functions χ_L can be expanded everywhere inside the circumscribed circle O in spherical harmonics:

$$V(\mathbf{r}) = \sum_L v_L(r) Y_L(\mathbf{r}), \quad \mathbf{r} \in O, \quad (13)$$

$$\chi_L(E, \mathbf{r}) = \frac{1}{r} \sum_{L'} \varphi_{L'L}(E, r) Y_{L'}(\hat{\mathbf{r}}), \quad \mathbf{r} \in O.$$

We determine the matrix elements of the potential:

$$v_{LL'}(r) = \int Y_L(\hat{\mathbf{r}}) V(\mathbf{r}) Y_{L'}(\hat{\mathbf{r}}) d\hat{\mathbf{r}}, \quad \mathbf{r} \in O. \quad (14)$$

The requirements that the function χ_L satisfy (12), be regular at zero, and be classified by the values of L lead then to a system of Volterra integral equations for $\varphi_{LL'}$ (Ref. 6):

$$\varphi_{LL'}(E, r) = \delta_{LL'} \tilde{f}_l(\kappa r) + \frac{1}{\kappa} \int_0^r [\tilde{n}_i(\kappa r_>) \tilde{f}_i(\kappa r_<) - \tilde{f}_i(\kappa r_>) \tilde{n}_i(\kappa r_<)]$$

$$\times \sum_{L''} v_{LL''}(r') \varphi_{L''L'}(E, r') dr',$$

$$r_< = \min(r, r'), \quad r_> = \max(r, r'), \quad \tilde{f}_i(x) = x j_i(x),$$

$$\tilde{n}_i(x) = x n_i(x). \quad (15)$$

Here $j_i(x)$ and $n_i(x)$ are Bessel and Neumann spherical functions, respectively, and $\kappa = E^{1/2}$. It is known that the functions χ_L (12) form a basis in the sense that the sought solution $\psi_{\mathbf{k}}$ can be expressed everywhere inside the cell Ω by the expansion²

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_L A_L(\mathbf{k}, E) \chi_L(E, \mathbf{r}), \quad \mathbf{r} \in \Omega. \quad (16)$$

We choose now an arbitrary point $\mathbf{r} \in D$ (see Fig. 1) and substitute the expansions (A6) and (16) in (11). Since the point \mathbf{r} belongs to the spherical region D , we can use the completeness of the set Y_L . Condition (11) takes then the form of a system of homogeneous algebraic equations in the unknown amplitudes A_L :

$$\sum_{L'} A_{L'}(\mathbf{k}, E) \left[\kappa g_{LL'}(\kappa) + \sum_{L''} B_{LL''}(\mathbf{k}, \kappa) f_{L''L'}(\kappa) \right] = 0, \quad (17)$$

where

$$f_{LL'}(\kappa) = \sum_{L''} \oint_{\sigma} d\sigma \{ [j_l(\kappa r) Y_L(\hat{\mathbf{r}})] \nabla [\varphi_{L''L'}(E, r) Y_{L''}(\hat{\mathbf{r}})/r] - [\varphi_{L''L'}(E, r) Y_{L''}(\hat{\mathbf{r}})/r] \nabla [j_l(\kappa r) Y_L(\hat{\mathbf{r}})] \}, \quad (18)$$

$$g_{LL'}(\kappa) = \sum_{L''} \oint_{\sigma} d\sigma \{ [n_l(\kappa r) Y_L(\hat{\mathbf{r}})] \nabla [\varphi_{L''L'}(E, r) Y_{L''}(\hat{\mathbf{r}})/r] - [\varphi_{L''L'}(E, r) Y_{L''}(\hat{\mathbf{r}})/r] \nabla [n_l(\kappa r) Y_L(\hat{\mathbf{r}})] \}.$$

The resultant secular equation

$$\det \left\| \kappa g_{LL'}(\kappa) + \sum_{L''} B_{LL''}(\mathbf{k}, \kappa) f_{L''L'}(\kappa) \right\| = 0 \quad (19)$$

determines the dispersion law $\kappa = \kappa(\mathbf{k})$ for the electron motion in a crystal with a potential $V(\mathbf{r})$ of arbitrary form.

Note that the matrices \mathbf{f} and \mathbf{g} depend only on the potential, while the matrix \mathbf{B} (A7) depends only on the lattice geometry and on the wave vector \mathbf{k} . This important property of the secular equation indicative of the KKR method in the MT model is thus realized in the general case.

4. PARTICULAR CASE OF AN MT POTENTIAL

Let us show that the system of equations (17) obtained for the general case is valid for an MT potential of form (3) or (4). It follows from the definitions (13) and (14) that in the case of an MT potential

$$u_{LL'}(r) = \delta_{LL'} u(r).$$

The system of coupled equations (15) breaks up into independent ones, and the functions $\varphi_{LL'}/r$ are solutions of the radial SE

$$\varphi_{LL'}(E, r)/r = \delta_{LL'} R_l(E, r),$$

$$\left[-\frac{1}{r^2} \frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + u(r) - E \right] R_l(E, r) = 0.$$

It can be shown with the aid of Green's theorem that since the potential $u(r)$ is equal to zero in the region $\Omega - \Omega^{\text{MT}}$, the integrals (18) over the cell surface σ are equal to integrals over the surface σ^{MT} of the MT sphere inscribed in the cell and having a radius b . Then

$$d\sigma^{\text{MT}} = \mathbf{e}_r r^2 d\hat{\mathbf{r}}$$

and

$$\nabla [p(r) Y_L(\hat{\mathbf{r}})] = \mathbf{e}_r Y_L(\hat{\mathbf{r}}) dp(r)/dr + \dots$$

Using the orthonormalizability of the spherical harmonics, we get

$$f_{LL'}^{\text{MT}}(\kappa) = \delta_{LL'} b^2 W[j_l(\kappa b), R_l(E, b)],$$

$$g_{LL'}^{\text{MT}}(\kappa) = \delta_{LL'} b^2 W[n_l(\kappa b), R_l(E, b)]. \quad (20)$$

We have introduced here the Wronskian defined by

$$W[p, q] = \left[p(r) \frac{dq(r)}{dr} - q(r) \frac{dp(r)}{dr} \right]_{r=b}.$$

Changing to the scattering phase shift $\eta_l(\kappa)$, which determines the asymptotic form of the solution R_l in the small δ -vicinity of the MT sphere:

$$R_l(E, r) = j_l(\kappa r) \cos \eta_l(\kappa) - n_l(\kappa r) \sin \eta_l(\kappa), \quad r > b - \delta,$$

we obtain the ratio of the Wronskians:

$$W[n_l, R_l]/W[j_l, R_l] = \text{ctg} \eta_l(\kappa). \quad (21)$$

Substituting (20) and (21) in the general secular equation (19) we obtain a particular form that is valid for the MT potential:

$$\det \left\| \delta_{LL'} \kappa \text{ctg} \eta_l(\kappa) + B_{LL'}(\mathbf{k}, \kappa) \right\| = 0. \quad (22)$$

Equation (22) coincides with the known result of the KKR theory.¹

5. NUMERICAL SOLUTION OF THE PROBLEM FOR A THREE-DIMENSIONAL PERIODIC MATHIEU POTENTIAL

It is expedient to check the method with model for which an exact solution is known. This is possible with the problem of the three-dimensional periodic Mathieu potential. We consider a simple cubic lattice with a potential

$$V(\mathbf{r}) = U_1 + U_2 [\cos(2\pi x/a) + \cos(2\pi y/a) + \cos(2\pi z/a)]. \quad (23)$$

The variables in the SE (1) are separable, and the energy eigenvalues of the three-dimensional problem can be obtained with the aid of the eigenvalues of the one-dimensional problem. The latter are determined as the roots of corresponding transcendental equations.⁷

The method developed (see Sec. 3) can be used to find the solutions at point Γ of the Brillouin zone (completely periodic solutions of the Mathieu problem). We expand the potential (23) in spherical harmonics. The components v_L (13) are equal to

$$v_L(r) = \begin{cases} 2\pi^{3/2} [U_1 + 3U_2 j_0(2\pi r/a)], & l=0, \\ 4\pi (-1)^{l/2} j_l(2\pi r/a) [Y_L(100) + Y_L(010) + Y_L(001)], & l - \text{even}, \\ 0, & l - \text{odd}, l=2. \end{cases} \quad (24)$$

To solve the system (15) of integral Volterra equations we use the phase-function (PF) method.² We define the PF:

$$C_{LL'}(r) = \delta_{LL'} - \frac{1}{\kappa} \int_0^r \tilde{n}_i(\kappa r') \sum_{L''} v_{LL''}(r') \varphi_{L''L'}(r') dr',$$

$$S_{LL'}(r) = \frac{1}{\kappa} \int_0^r \tilde{j}_i(\kappa r') \sum_{L''} v_{LL''}(r') \varphi_{L''L'}(r') dr'. \quad (25)$$

Equation (15) takes then the form

$$\varphi_{LL'}(E, r) = C_{LL'}(r) \tilde{j}_i(\kappa r) + S_{LL'}(r) \tilde{n}_i(\kappa r), \quad (26)$$

and the PF (25) satisfy the system of coupled equations

$$\frac{dC_{LL'}}{dr} = -\frac{1}{\kappa} \tilde{n}_i(\kappa r) \sum_{L''} v_{LL''}(r) [\tilde{j}_{L''}(r) C_{L''L'}(r) + \tilde{n}_{L''}(r) S_{L''L'}(r)],$$

$$\frac{dS_{LL'}}{dr} = \frac{1}{\kappa} \tilde{j}_i(\kappa r) \sum_{L''} v_{LL''}(r) [\tilde{j}_{L''}(r) C_{L''L'}(r) + \tilde{n}_{L''}(r) S_{L''L'}(r)] \quad (27)$$

and the boundary conditions

$$C_{LL'}(0) = \delta_{LL'}, \quad S_{LL'}(0) = 0.$$

In (26) and (27) we have $0 < r < c$, where $c = a\sqrt{3}/2$ is the radius of the inscribed sphere. The system (27) of first-order equation was solved by the Runge-Kutta method. The PF obtained, $C_{LL'}$ and $S_{LL'}$, allow us to calculate the $\varphi_{LL'}$ (26) and obtain on their basis the integrals (18).

To obtain symmetrized (in accordance with the irreducible representations of the point Γ) combinations of basis functions and symmetrized integrands in (18) we used the system of analytic symbolic programming.⁸ The maximum values L_{\max} of the angular momenta in the expansion (6) are equal to 10 for the representation Γ_1 and to 7 for the representation Γ_{15} . The dimensionalities of the corresponding secular matrices are equal to 5 (Γ_1) and 6 (Γ_{15}). To calculate the GF expansion coefficients $B_{LL'}$ (A7) we used Ewald's method.⁹ The solution of the secular equation (10) calls for

finding the zeros of the determinant as a function of energy.

The calculations were performed for a certain set of values of the parameter U_2 of the model potential (23) for a lattice parameter $a = \pi$. It is also convenient to change to dimensionless energy units $\varepsilon = Ea^2/4\pi^2$. In Table I the calculated energies of the bands $1\Gamma_1$ and $1\Gamma_{15}$ are compared with the exact analytic values.

Note that a relatively small number of basis functions suffices for quite satisfactory accuracy. Thus, in a wide range of the parameter U_2 the deviation of the calculated energy eigenvalue from the exact one does not exceed 0.003 (in dimensionless ε units). The rate of convergence relative to the number of basis functions included in the expansion (6) and determined by the value of l_{\max} can be demonstrated with the Γ_{15} bands as an example (Table II). Owing to the variational character of the method, the energy eigenvalues determined by a specified number of basis functions can be higher as well as lower than the limiting exact value. The convergence is therefore not uniform.

Nevertheless, it is clear even now that the required values of l_{\max} are considerably larger than those customarily used in the MT model. It is known that in the case of an MT potential a value $l_{\max} = 2$ ensures a relative energy accuracy ≈ 0.001 in the calculation of the occupied states of crystals consisting of atoms of the first half of the periodic table. Values $l_{\max} = 3$ to 4 are needed only for crystals containing atoms with f shells. The increase of l_{\max} compared with the MT case is a natural price to pay for taking into account a potential with a more complicated relief.

Our numerical analysis of the Mathieu equation is the first ever. The approaches mentioned in Sec. 2, based on the concept of multiple scattering, were tested only with the aid of the case of an "empty lattice," i.e., for $V(r) = U_1$. This potential can be regarded as a particular case of a Mathieu equation at $U_2 = 0$. The results of application of the method to the "empty lattice" case are given in Ref. 10.

6. CONCLUSIONS

The formalism considered is intended for calculations of the electron structure of crystals described by an effective potential of arbitrary form. It yields a rigorous (nonvariational) solution of the problem of finding Bloch functions. The method can be used for arbitrary crystals with different types of chemical bond. For the particular case of MT potentials the formalism reduces to the known method of the KKR band theory.¹

A similar generalization is possible also for the electron

TABLE I. Energy eigenvalues ε of bands $1\Gamma_1$ and $1\Gamma_{15}$ for the three-dimensional periodic Mathieu potential (23) ($U_1 = -0.4$; $a = \pi$).

U_2	$1\Gamma_1$		$1\Gamma_{15}$	
	Calculation (19)	Exact value	Calculation (19)	Exact value
-0.4	-0.115	-0.115	0.889	0.889
-0.8	-0.160	-0.159	0.858	0.857
-1.2	-0.233	-0.230	0.807	0.806
-1.6	-0.328	-0.325	0.738	0.737
-2.0	-0.443	-0.441	0.654	0.652
-2.4	-	-	0.556	0.554
-2.8	-	-	0.446	0.444
-3.2	-	-	0.326	0.324
-3.6	-	-	0.197	0.196
-4.0	-	-	0.0612	0.0611

TABLE II. Convergence of energy eigenvalues ε of Γ_{15} symmetry.

U_2	Calculation (19)			Exact value
	$l_{max}=1$	$l_{max}=3$	$l_{max}=5$	
-2.4	0.59	0.72	0.556	0.554
-3.2	0.40	0.39	0.326	0.324
-4.0	0.17	0.08	0.0612	0.0611

structure of molecules and clusters.¹¹ In this case the formalism for MT potential reduces to known Slater-Johnson scattered-waves method.¹²

From the fundamental point of view, the method is preferable because it yields a final solution of an *ab initio* single-particle problem. From the physical point of view the method is needed in cases when the potential-anisotropy effects are so strong that the MT approximation can lead to results that are incorrect both quantitatively and qualitatively. Let us name some of these problems.

It is known from molecular theory that the MT approximation leads to considerable errors in the determination of the total energy of a molecule. The method developed here can be used to calculate the total-energy surfaces as functions of the nuclear coordinates, and hence determine the vibrational spectra of the molecules.

In the theory of the electron structure of crystals, the largest anisotropy effects should be expected for covalent crystals, and also for compounds with a chemical bond of the coordination type, including complex oxides in the class of high-temperature superconductors. At the present time the main results for covalent crystals were obtained by LCAO and pseudopotential variational methods, and in the case of high-temperature superconductors with the aid of the LMTO method with an MT potential. A proper allowance for the anisotropy of the crystal potential can lead to a change of the dispersion law of the electrons and of the shape of the Fermi surface, and can consequently influence the model premises based on results of calculations in the MT approximation.

APPENDIX

Two-center expansion of the Green's function for a crystal

The Green's function (GF) (6) of an empty lattice satisfies the inhomogeneous equations

$$(\nabla^2 + E)G_{\mathbf{k}}(\mathbf{r}, \mathbf{r}'; E) = (\nabla'^2 + E)G_{\mathbf{k}}(\mathbf{r}, \mathbf{r}'; E) = \delta(\mathbf{r} - \mathbf{r}') \quad (\text{A1})$$

and periodic boundary conditions. It is an analytic function of the energy E , and its values on the real axis, except at the points $E_{\mu} = |\mathbf{k} + \mathbf{K}_{\mu}|^2$, can be obtained by analytic continuation from the complex plane. It follows from (A1) that the GF can be expanded in solutions of the corresponding homogeneous Helmholtz equations. Let us find this expansion.

The GF is periodic in reciprocal space. It can consequently be represented by a Fourier series over the direct lattice:

$$G_{\mathbf{k}}(\mathbf{r}, \mathbf{r}'; E) = \sum_{\mathbf{R}_n} f_n \exp(i\mathbf{k}\mathbf{R}_n). \quad (\text{A2})$$

The expansion coefficients are

$$f_n = -\frac{1}{(2\pi)^3} \sum_{\mathbf{k}_{\mu}} \int d^3k \frac{\exp[i(\mathbf{k} + \mathbf{K}_{\mu})(\mathbf{r} - \mathbf{r}')] \exp(-i\mathbf{k}\mathbf{R}_n)}{|\mathbf{k} + \mathbf{K}_{\mu}|^2 - E}$$

(the integral is taken over the Brillouin zone). We introduce the vector $\mathbf{q} = \mathbf{k} + \mathbf{k}_{\mu}$. We have then

$$f_n = -\frac{1}{(2\pi)^3} \int \int \int_{-\infty}^{\infty} d^3q \frac{\exp[i\mathbf{q}(\mathbf{r} - \mathbf{r}' - \mathbf{R}_n)]}{q^2 - E}.$$

Using the expansion of a plane wave in real spherical harmonics Y_L we get

$$f_n = 8 \sum_{L, L', L''} i^{l-l'-l''} Y_L(\hat{\mathbf{r}}) Y_{L'}(\hat{\mathbf{r}}') Y_{L''}(\hat{\mathbf{R}}_n) (L, L', L'') \times \int_0^{\infty} \frac{j_l(qr) j_{l'}(qr') j_{l''}(qR_n)}{E - q^2} q^2 dq, \quad (\text{A3})$$

where

$$(L, L', L'') \equiv \int Y_L(\hat{\mathbf{q}}) Y_{L'}(\hat{\mathbf{q}}) Y_{L''}(\hat{\mathbf{q}}) d\hat{\mathbf{q}}.$$

The integrals

$$I_n \equiv \int_0^{\infty} \frac{j_l(qr) j_{l'}(qr') j_{l''}(qR_n)}{E - q^2} q^2 dq$$

can be calculated by residue theory. If $r < r'$ and

$$r + r' < R_n, \quad R_n \neq 0, \quad (\text{A4})$$

the conditions of the Jordan lemma are met and the integrals are equal to

$$I_0 = -1/2 i \kappa \pi j_l(\kappa r) h_l^{(4)}(\kappa r'), \quad r < r', \quad R_n = 0,$$

$$I_n = -1/2 i \kappa \pi j_l(\kappa r) j_{l'}(\kappa r') h_l^{(4)}(\kappa R_n), \quad r + r' < R_n, \quad R_n \neq 0. \quad (\text{A5})$$

Here $\kappa = E^{1/2}$ and $h_l^{(1)}(x)$ are spherical Hankel functions of the first kind.

With the aid of (A2), (A3), and (A5) we obtain the sought two-center expansion of the GF⁹

$$G_{\mathbf{k}}(\mathbf{r}, \mathbf{r}'; E) = \kappa \sum_L j_l(\kappa r) n_l(\kappa r') Y_L(\mathbf{r}) Y_L(\mathbf{r}') \quad (\text{A6})$$

$$+ \sum_{L, L'} B_{LL'}(\mathbf{k}, E) j_l(\kappa r) j_{l'}(\kappa r') Y_L(\mathbf{r}) Y_{L'}(\hat{\mathbf{r}}'),$$

$$r < r', \quad r + r' < R_n.$$

The expansion coefficients

$$B_{LL'}(\mathbf{k}, E) = 4\pi i^{l-l'} \sum_{L''} (L, L', L'') D_{L''}(\mathbf{k}, E) \quad (\text{A7})$$

are expressed in terms of the so-called structure constants

$$D_L(\mathbf{k}, E)$$

$$= -i^{-l} (i\kappa) \left[\frac{\delta_{Lo}}{2\pi^{3/2}} + \sum_{\mathbf{R}_n \neq 0} h_l^{(4)}(\kappa R_n) Y_L(\hat{\mathbf{R}}_n) \exp(i\mathbf{k}\mathbf{R}_n) \right].$$

If, however, inequality (A4) is not satisfied, other expansions are valid. For example, if

$$r + R_n < r', \quad (\text{A8})$$

then

$$G_{\mathbf{k}}(\mathbf{r}, \mathbf{r}'; E) = \kappa \sum_{\mathbf{L}} j_l(\kappa r) n_l(\kappa r') Y_L(\hat{\mathbf{r}}) Y_L(\hat{\mathbf{r}}') + \sum_{L, L'} \tilde{B}_{LL'}(\mathbf{k}, E) j_l(\kappa r) h_l^{(4)}(\kappa r') Y_L(\hat{\mathbf{r}}) Y_{L'}(\hat{\mathbf{r}}'), \quad r < r', \quad r + R_n < r', \quad (\text{A9})$$

where

$$\tilde{B}_{LL'}(\mathbf{k}, E) = 4\pi i^{l-l'} \sum_{L''} (L, L', L'') \tilde{D}_{L''}(\mathbf{k}, E),$$

$$\tilde{D}_L(\mathbf{k}, E) = -i^{-l} (i\kappa) \left[\frac{\delta_{Lo}}{2\pi^{3/2}} + \sum_{\mathbf{R}_n \neq 0} j_l(\kappa R_n) Y_L(\hat{\mathbf{R}}_n) \exp(i\mathbf{k}\mathbf{R}_n) \right].$$

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