

Full-potential Korringa-Kohn-Rostoker band theory applied to the Mathieu potential

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The band theory of Korringa, Kohn, and Rostoker (KKR) based on the Green-function method is extended to space-filling potentials. A numerical test using the Mathieu potential shows good convergence for the bands up to 1.5 Ry with $l \leq 4$ included in the angular-momentum expansion for the wave functions. Our results strongly support the applicability of the full-potential KKR to bulk electronic-structure problems.

I. INTRODUCTION

The Korringa, Kohn, and Rostoker (KKR) band theory¹⁻² is an elegant theory for the one-electron energy bands in a closed-packed crystal for which the muffin-tin (MT) construction for the potential is a reasonable approximation. To expand the scope of application, considerable effort has been expended to extend the KKR theory to full crystal potentials.³⁻¹¹ One concern about such extension is related to the so-called near-field corrections (NFC) (Refs. 3-5) arising from the expansion of the KKR Green function beyond the muffin-tin region. Although there are proofs^{7,9,11} showing that NFC do not exist, questions have been raised about the applicability of the theory.¹² Since space-filling potentials are non-spherical and the Wigner-Seitz cell boundary is not smooth, we are further concerned about the speed of convergence in terms of angular-momentum (l) expansions. In this paper the integral equation approach of Kohn and Rostoker² (KR) is used to derive the full-potential KKR (FP-KKR) equation explicitly. One advantage of our derivation is that all the quantities involved are functions of \mathbf{r} within a unit cell. Thus we can avoid the uncertainty in extending the wave function beyond the unit cell encountered in some other derivations.^{6,11} We have also tested the convergence by comparing the numerical results with the exact solution for the Mathieu potential¹³⁻¹⁵ in the simple-cubic crystal. Excellent results for the band structure in the energy range of interest are obtained with a maximum value of $l = 4$ included in this expansion.

The fact that the Mathieu potential is exactly soluble gives it an advantage for testing purposes over working with realistic potentials.^{4,9,17} Our test complements the empty-lattice potential¹⁸⁻²⁰ to provide a stringent test for the FP-KKR theory. The strong angular-momentum dependence in the Mathieu potential gives a good representation of the anisotropy that is present in the open structures pertaining to many semiconductors and insulators. The restriction of the KKR to closed-packed metals imposed by the muffin-tin approximation is lifted by

the full-potential method discussed here. The results obtained here should encourage the application of this theory to real crystals.

II. THE FULL-POTENTIAL KKR EQUATION

In this section we want to show that the Kohn-Rostoker integral equation can be simply extended to obtain the full potential KKR theory. The Schrödinger equation in the band calculation

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

for a full crystal potential $V(\mathbf{r})$ is equivalent to solving the following integral equation:²

$$\psi_{\mathbf{k}}(E, \mathbf{r}) = \int_{\tau} G_{\mathbf{k}}(E; \mathbf{r}, \mathbf{r}') V(\mathbf{r}') \psi_{\mathbf{k}}(E, \mathbf{r}') d\mathbf{r}', \quad (2)$$

where the integration is over the Wigner-Seitz cell of volume τ , and \mathbf{k} is a crystal wave vector. $G_{\mathbf{k}}(E; \mathbf{r}, \mathbf{r}')$ in Eq. (3) is the KKR free-electron Green's function²

$$G_{\mathbf{k}}(E; \mathbf{r}, \mathbf{r}') = -\frac{1}{\tau} \sum_n \frac{\exp[i(\mathbf{K}_n + \mathbf{k}) \cdot (\mathbf{r} - \mathbf{r}')] }{(\mathbf{K}_n + \mathbf{k})^2 - E}, \quad (3)$$

where \mathbf{K}_n are the reciprocal-lattice vectors. Alternatively $G_{\mathbf{k}}(E; \mathbf{r}, \mathbf{r}')$ can be expressed as²

$$G_{\mathbf{k}}(E; \mathbf{r}, \mathbf{r}') = -\frac{1}{4\pi} \sum_s \frac{\exp(i\kappa|\mathbf{r} - \mathbf{r}' - \mathbf{R}_s|)}{|\mathbf{r} - \mathbf{r}' - \mathbf{R}_s|} \exp(i\mathbf{k} \cdot \mathbf{R}_s), \quad (4)$$

where $\kappa = \sqrt{E}$ for $E > 0$ and $\kappa = i\sqrt{|E|}$ for $E < 0$, and \mathbf{R}_s are the lattice translation vectors. To derive the FP-KKR equation, we first observe that Eq. (3) can be cast into a surface integral,

$$\int_{S_{\tau}} [G_{\mathbf{k}}(E; \mathbf{r}, \mathbf{r}') \nabla' \psi_{\mathbf{k}}(E, \mathbf{r}') - \psi_{\mathbf{k}}(E, \mathbf{r}') \nabla' G_{\mathbf{k}}(E; \mathbf{r}, \mathbf{r}')] \cdot d\mathbf{S}' = 0, \quad (5)$$

where S_{τ} is the surface of the Wigner-Seitz cell.

Since the $|\mathbf{r}'|$ in the surface integral exceeds the muffin-tin radius r_m , we need to consider the expansion of

the Green function beyond the original range of Kohn and Rostoker. Several authors have already considered this point. For simplicity, we shall only consider the case with one atom per unit cell. Since this expansion is a cen-

tral point of controversy, we rederive the results explicitly in the Appendix for the range of \mathbf{r} and \mathbf{r}' needed here. We show that the expansion

$$G_{\mathbf{k}}(E; \mathbf{r}, \mathbf{r}') = \sum_L \left[\sum_{L'} [i^{(l-l')} B_{L,L'}(\mathbf{k}, E) J_L(\kappa \mathbf{r}) J_{L'}(\kappa \mathbf{r}') + \kappa \delta_{LL'} J_L(\kappa \mathbf{r}) N_{L'}(\kappa \mathbf{r}')] \right] \quad (6)$$

is valid as long as both \mathbf{r} and \mathbf{r}' are inside τ and satisfy the following condition:

$$|\mathbf{r}| < |\mathbf{r}'| < |\mathbf{R}_s| \quad \text{for all } |\mathbf{R}_s| \neq 0. \quad (7)$$

In Eq. (6) the notations $J_L(\kappa \mathbf{r}) = j_l(\kappa r) Y_L(\mathbf{r})$ and $N_L(\kappa \mathbf{r}) = n_l(\kappa r) Y_L(\mathbf{r})$ are used, where j_l and n_l are, respectively, the spherical Bessel and Neumann functions, Y_L is a real spherical harmonics, and L represents the double indices (l, m) . $B_{L,L'}(\mathbf{k}, E)$ is the usual KKR structure constant.^{2,13} We note that for any $|\mathbf{r}|$ smaller than r_m , the condition in Eq. (7) is satisfied for all \mathbf{r}' contributing to the surface integration in Eq. (5). The condition $|\mathbf{r}'| < |\mathbf{R}_s|$ in Eq. (7) holds for most lattices; exceptions are those, for example, with long narrow cells. For such cases, this condition can be satisfied by breaking the unit cell into smaller cells including so-called "empty cells" which do not contain an atomic nucleus.

The wave function inside the cell τ can be expanded in a basis set $\{\Phi_L(E, \mathbf{r})\}$ as

$$\psi_{\mathbf{k}}(E, \mathbf{r}) = \sum_L a_L(\mathbf{k}, E) \Phi_L(E, \mathbf{r}). \quad (8)$$

The basis function $\Phi_L(E, \mathbf{r})$ is a regular solution to the Schrödinger equation inside τ ,

$$[-\nabla^2 + V(\mathbf{r})] \Phi_L(E, \mathbf{r}) = E \Phi_L(E, \mathbf{r}), \quad (9)$$

and behaves like $J_L(\kappa \mathbf{r})$ at the origin $r = r_0 \rightarrow 0$, which is typically the location of the atomic nucleus. This basis set can be calculated using the following integral equation:⁴

$$\Phi_L(E, \mathbf{r}) = J_L(\kappa \mathbf{r}) + \sum_{L'} \int_{r_0}^r g_{L'}(E; \mathbf{r}, \mathbf{r}') V(\mathbf{r}') \Phi_{L'}(E, \mathbf{r}') d^3 r', \quad (10)$$

where $g_L(E; \mathbf{r}, \mathbf{r}')$ is a free-particle Green's function and is defined as

$$g_L(E; \mathbf{r}, \mathbf{r}') = \kappa [J_L(\kappa \mathbf{r}) N_L(\kappa \mathbf{r}') - N_L(\kappa \mathbf{r}) J_L(\kappa \mathbf{r}')] . \quad (11)$$

We note that the basis function $\Phi_L(E, \mathbf{r})$ is coupled to other angular-momentum channels for $r > r_0$, because the crystal potential $V(\mathbf{r})$ is not spherical.

The expansions of G in Eq. (6) and of ψ in Eq. (8) can be substituted in Eq. (5) to obtain

$$\sum_L J_L(\kappa \mathbf{r}) \sum_{L''} \left[\left[\sum_{L'} i^{(l-l')} B_{L,L'}(\mathbf{k}, E) S_{L',L''}(E) \right] + \kappa C_{L,L''}(E) \right] a_{L''}(\mathbf{k}, E) = 0, \quad r < r_m, \quad (12)$$

where

$$S_{L',L''}(E) = \kappa \int_{S_\tau} [J_{L'}(\kappa \mathbf{r}'), \Phi_{L''}(E, \mathbf{r}')] \cdot d\mathbf{S}', \quad (13)$$

and

$$C_{L,L''}(E) = \kappa \int_{S_\tau} [N_L(\kappa \mathbf{r}'), \Phi_{L''}(E, \mathbf{r}')] \cdot d\mathbf{S}'. \quad (14)$$

In the above, the notation $[F_1, F_2] \equiv F_1 \nabla F_2 - F_2 \nabla F_1$ has been used. The surface integrals in Eqs. (13) and (14) are over the boundaries of τ as indicated by S_τ . Since $J_L(\kappa \mathbf{r})$ in Eq. (12) are linearly independent functions, the following set of homogeneous equations holds:

$$\sum_{L''} \left[\left[\sum_{L'} i^{l-l'} B_{L,L'}(\mathbf{k}, E) S_{L',L''}(E) \right] + \kappa C_{L,L''}(E) \right] a_{L''}(\mathbf{k}, E) = 0. \quad (15)$$

This is the FP-KKR equation that we are after.

We note that our derivation is similar to Nesbet's derivation.¹¹ We hope, however, that the above explicit derivation may be more accessible to some readers. It is also useful for establishing the notation necessary for the description of the application of FP-KKR theory to the solution of the Mathieu potential which constitutes the main result of this paper.

III. CALCULATION OF S AND C MATRICES

The surface integrals for the S and C matrices in Eqs. (13) and (14) can be very time consuming. It is desirable to seek simplification of these calculations in a real application. One plausible approximation which is consistent with the KKR spirit is to expand every quantity involved in angular-momentum components. Equations (13) and (14) are equivalent to the volume integrations

$$S_{L',L}(E) = \kappa \int_\tau J_{L'}(\kappa \mathbf{r}) V(\mathbf{r}) \Phi_L(E, \mathbf{r}) d\mathbf{r} \quad (16)$$

and

$$C_{L'L}(E) = -\delta_{L,L'} + \kappa \int_{\tau} N_{L'}(\kappa \mathbf{r}) V(\mathbf{r}) \Phi_L(E, \mathbf{r}) d\mathbf{r}. \quad (17)$$

One can free the limits of these integrals by replacing the crystal potential V by the truncated potential V^T ,

$$V^T(\mathbf{r}) = V(\mathbf{r}) \sigma(\mathbf{r}), \quad (18)$$

where $\sigma(\mathbf{r})$ is a step function and is defined as

$$\sigma(\mathbf{r}) = \begin{cases} 1, & \text{for } \mathbf{r} \text{ within } \tau \\ 0, & \text{otherwise.} \end{cases} \quad (19)$$

The angular-momentum expansion for the basis function is assumed to be

$$\Phi_L(E, \mathbf{r}) = \sum_{L'} \phi_{L'L}(E, r) Y_{L'}(\mathbf{r}), \quad (20)$$

and the truncated potential V^T is expanded as

$$V^T(\mathbf{r}) = \sum_L V_L^T(r) Y_L(\mathbf{r}). \quad (21)$$

The integrations in Eqs. (16) and (17) can be reduced, respectively, to the simple radial integrations

$$S_{L'L}(E) = \kappa \sum_{L''} \int_{r_0}^{r_s} j_{L'}(\kappa r) V_{L'L''}(r) \phi_{L''L}(E, r) r^2 dr \quad (22)$$

and

$$C_{L'L}(E) = -\delta_{L,L'} + \kappa \sum_{L''} \int_{r_0}^{r_s} n_{L'}(\kappa r) V_{L'L''}(r) \times \phi_{L''L}(E, r) r^2 dr, \quad (23)$$

where r_s is the radius of the circumscribing sphere of the Wigner-Seitz cell. The $V_{L'L''}(r)$ is given by

$$\begin{aligned} V_{L'L''}(r) &= \int Y_{L'}(\mathbf{r}) V^T(\mathbf{r}) Y_{L''}(\mathbf{r}) d\Omega \\ &= \sum_L C_{L'L''}^L V_L^T(r), \end{aligned} \quad (24)$$

where

$$C_{L'L''}^L \equiv \int Y_{L'}(\mathbf{r}) Y_L(\mathbf{r}) Y_{L''}(\mathbf{r}) d\Omega \quad (25)$$

is a Gaunt coefficient.

Note that in the above the basis function $\Phi_L(E, \mathbf{r})$ is assumed to be calculated from Eq. (10), where $V(\mathbf{r})$ is the full crystal potential. This is the same procedure used by Brown and Ciftan (BC).⁶ The original Williams-Morgan³ (WM) approach, however, used the truncated potential V^T for the calculation of the basis function in Eq. (10). If expansions of the potential and Φ_L in Eq. (10) include all the angular-momentum components, both approaches probably will give the same results for the band structure, provided both converge.^{11,21} In practice, the expansion is limited to a certain l_{\max} ; therefore, these two approaches yield different results.

In the actual calculation of the basis functions using either V or V^T , we first write the potential as the sum of V_0 and ΔV , where V_0 is the spherical part of the potential and ΔV is the rest. We then solve for the radial wave function f_l corresponding to V_0 . Similarly, the basis is written as $\Phi_L = F_L + \Delta\Phi_L$, where $F_L = f_L Y_L$, and $\Delta\Phi_L$ is solved from the integral equation

$$\begin{aligned} \Delta\Phi_L(E; r) &= \sum_{L'} \int_{r_0}^r g_{L'}(E; \mathbf{r}, \mathbf{r}') \Delta V(\mathbf{r}') F_L(E; \mathbf{r}') d\mathbf{r}' \\ &+ \sum_{L'} \int_{r_0}^r g_{L'}(E; \mathbf{r}, \mathbf{r}') V(\mathbf{r}') \Delta\Phi_L(E; \mathbf{r}') d\mathbf{r}', \end{aligned} \quad (26)$$

iteratively using angular-momentum expansions for all quantities involved.

IV. APPLICATION TO MATHIEU POTENTIAL

To test the accuracy of the FP-KKR equation and the convergence in angular expansion described above, we applied the theory to the Mathieu potential¹³⁻¹⁶ of the form

$$V(\mathbf{r}) = -U_0 \left[\cos \frac{2\pi x}{\alpha} + \cos \frac{2\pi y}{\alpha} + \cos \frac{2\pi z}{\alpha} \right], \quad (27)$$

where we took the lattice constant α to be 2π times the Bohr radius and the potential parameter U_0 to be 0.5 Ry. Because the potential is separable, the eigenvalue problem reduces to three one-dimensional problems. The band structures and corresponding wave functions can be computed to the precision of the computer and can be regarded as "exact" in the numerical comparison.

The Mathieu potential is poorly represented by the MT approximation, because the simple cubic structure is rather open and the potential has a large variation in the

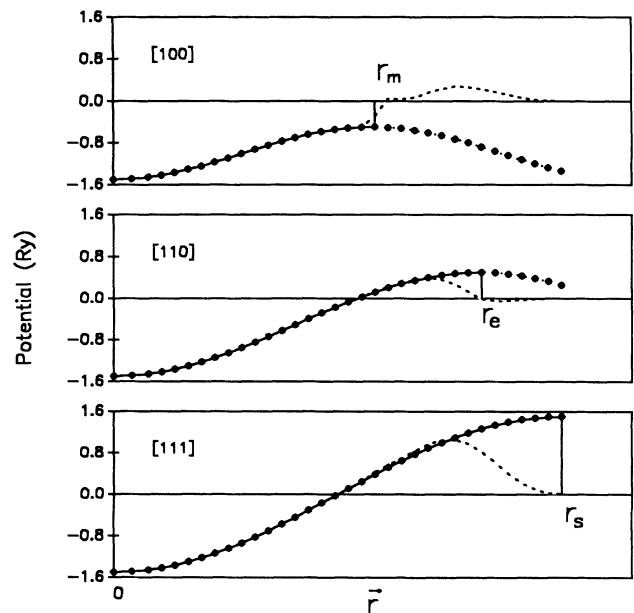


FIG. 1. Angular-momentum expansion of the Mathieu potential along [100], [110], and [111]. The solid circles represent the continuous crystal potential $V(\mathbf{r})$, and the solid lines are the truncated potential $V^T(\mathbf{r})$. The dotted and the dashed lines are the sums of the angular-momentum components up to $l=8$ for $V(\mathbf{r})$ and $V^T(\mathbf{r})$, respectively. r_m , r_e , and r_s are the distances between the origin and the face, edge, and corner of the cube, respectively. Notice that the dotted line and the solid circles are not distinguishable in the figure.

interstitial region. For example, with U_0 set to be 0.5 Ry, the MT constant potential is $V_c = U_0[9/\pi(6-\pi)] \approx 0.501116$ Ry, while the actual value of the potential varies from -0.5 Ry at $(\frac{1}{2}, 0, 0)\alpha$ to 1.5 Ry at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})\alpha$.

When the full potential in Eq. (27) is expanded in cubic harmonics $V(\mathbf{r}) = \sum_L V_L(r)K_L(\mathbf{r})$, $V_L(r)$ is proportional to $-U_0 j_l(2\pi r/\alpha)$, and the series converges very fast. With an $l_{\max} = 8$, one can achieve a converged $V(\mathbf{r})$, as shown in Fig. 1. However, in the expansion for the truncated potential, $V^T(\mathbf{r}) = V(\mathbf{r})\sigma(\mathbf{r}) = \sum_L V_L^T(r)K_L(\mathbf{r})$, the components

$$V_L^T(r) = \int K_L(\mathbf{r})V(\mathbf{r})\sigma(\mathbf{r})d\mathbf{r} \quad (28)$$

have to be carried out numerically with great care. Be-

cause of sharp edges and corners in $V^T(\mathbf{r})$, the angular-momentum expansion is only slowly converging. This is evident in Fig. 1, which shows sizable errors made in all three directions [100], [110], and [111] in the expansion of V^T up to $l_{\max} = 8$.

We have carried out the FP-KKR calculation using the wave-function expansion in Eqs. (10) and (24) up to $l_{\max} = 4$. The basis sets are calculated using both the BC and WM approaches with the potentials expanded up to $l_{\max} = 8$. Results from the MT-KKR approximation are also obtained for comparison.

In Fig. 2(a), the solid lines represent the "exact" band structures for the Mathieu potential. The dots are the MT-KKR results. Despite the crude approximation in the MT potential, the lowest band is still reasonable. The MT approximation becomes worse at the higher energies,

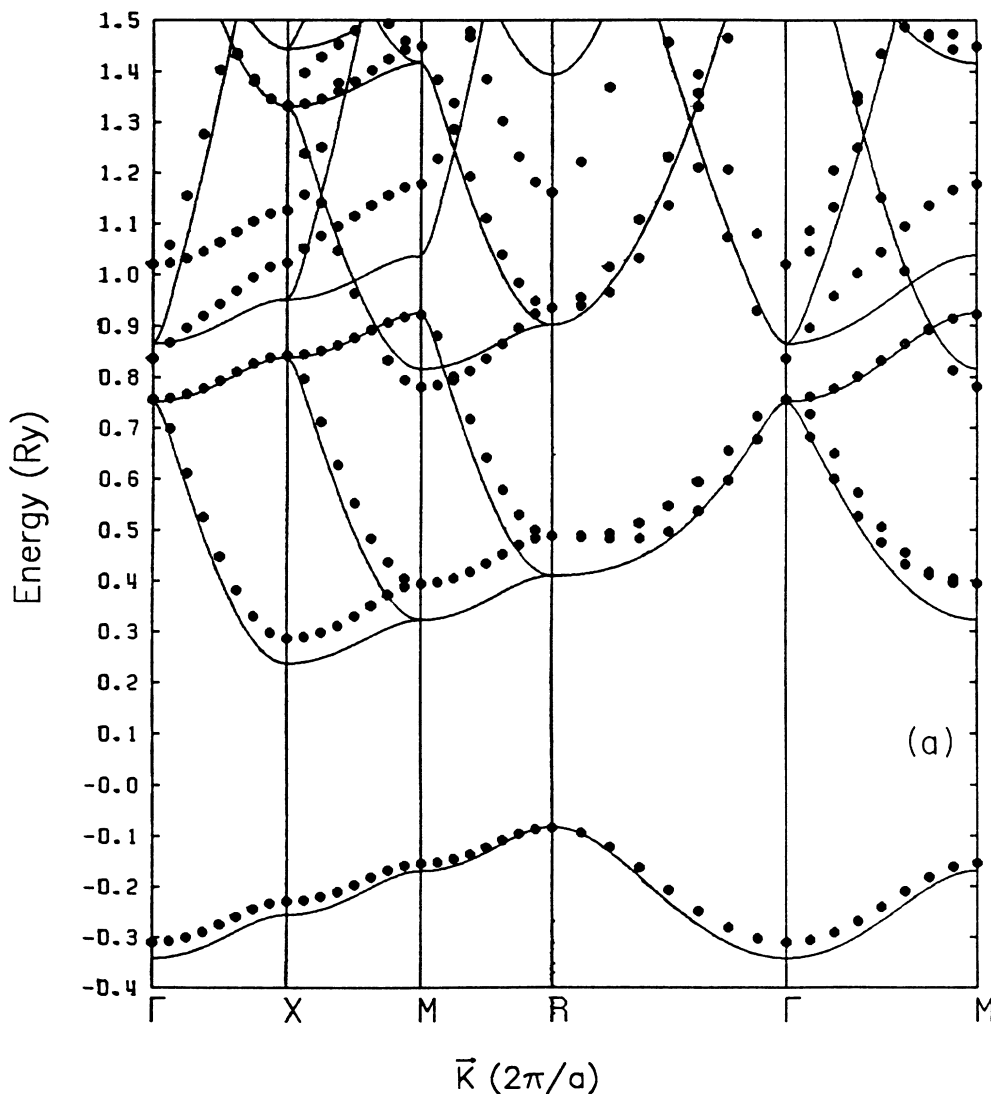


FIG. 2. Comparison of (a) the muffin-tin KKR and (b) the FP-KKR band structures (the dots) with the exact results (the solid lines) for the Mathieu potential. The symmetry points Γ , X , M , and R correspond to the wave vector at $(0,0,0)$, $(\frac{1}{2}, 0, 0)$, $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, respectively, in units of $2\pi/a$.

as indicated by the large energy deviations and splittings of the levels. For example, the "exact" bands from Γ to X from Γ to M around 0.9 Ry are degenerate due to separability of the Mathieu potential, while the MT approximation lifts this "accidental" degeneracy.

The full-potential KKR results are compared with the "exact" band structure in Fig. 2(b). The dots are now the FP-KKR results and are calculated based on the BC approach. The agreement is excellent and rather uniform up to 1.3 Ry. The calculation even preserves the accidental degeneracy at Γ at energy 0.88 Ry. The lowest band has a detectable deviation of 0.016 Ry at R , but has very small root-mean-square (rms) deviation. The deviations at R and some other energy states are probably due to the truncation in the angular-momentum expansions. The FP-KKR bands based on the WM approach are not no-

ticeably different from those based on the BC approach plotted in Fig. 2(b). However, there are slight differences between the results of the two approaches. For reference, we list the deviations of both the BC and WM approaches and the "exact" energies in Table I. While the WM approach gives a larger deviation in the lowest-energy band around R , the overall rms deviations of these two approaches are similarly small. These results imply some freedom in the choice of basis functions. Provided that reasonable approximations are made in the representation of the cell potential V^T and in the calculation of $S_{LL'}$ and $C_{LL'}$ from Eqs. (21) and (22), it appears that the FP-KKR equation will give reasonable bands independent of the exact algorithm for obtaining the Φ_L , e.g., from $V(\mathbf{r})$, $V^T(\mathbf{r})$, or other smooth potentials augmented to V^T .

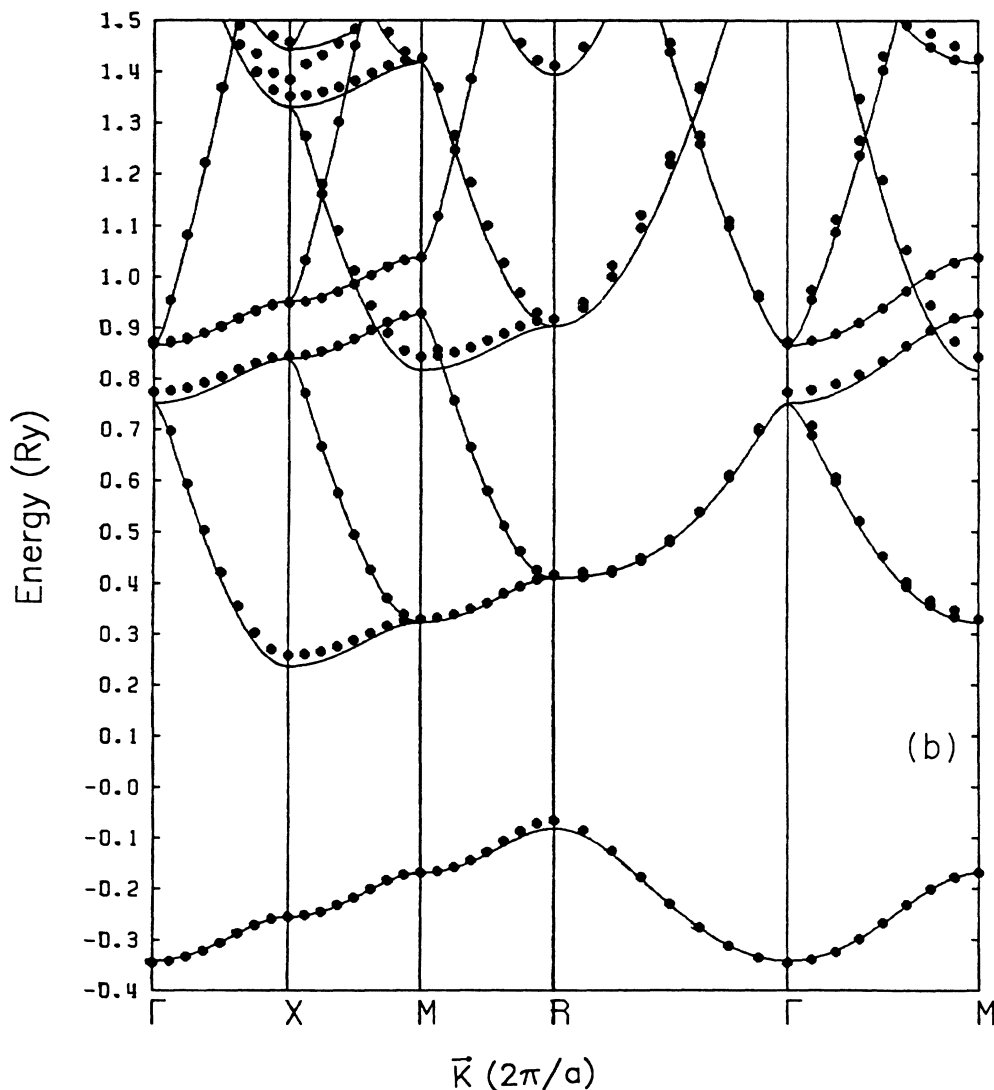


FIG. 2. (Continued).

TABLE I. Deviations of the FP-KKR band energies ΔE from the exact values E_{exact} for the Mathieu potential at several symmetry points. The subscripts WM and BC stand, respectively, for the Williams-Morgan and Brown-Ciftan approaches described in the text. All energies are in Ry.

Symmetry states	ΔE_{WM}	ΔE_{BC}	E_{extract}
Γ_1	-0.0053	-0.0034	-0.3414
Γ_{15}	0.0243	0.0223	0.7517
Γ_1	-0.0015	0.0024	0.8653
Γ_{12}	0.0034	0.0069	0.8653
R_1	0.0274	0.0160	-0.0827
R_{15}	0.0089	0.0064	0.4097
$R_{25'}$	0.0156	0.0145	0.9020
$R_{2'}$	0.0184	0.0171	1.3943
X_1	0.0024	0.0005	-0.2551
$X_{4'}$	0.0214	0.0216	0.2372
$X_{5'}$	0.0060	0.0056	0.8379
X_1	-0.0010	-0.0021	0.9515
X_2	-0.0047	-0.0036	0.9515
M_1	0.0016	0.0002	-0.1689
$M_{5'}$	0.0072	0.0067	0.3234
M_3	0.0270	0.0259	0.8158
$M_{4'}$	0.0033	0.0037	0.9241
M_1	0.0058	-0.0005	1.0377

V. SUMMARY

The main purpose of this paper is to test the accuracy of the FP-KKR theory in band-structure calculations. To help eliminate doubts about this theory, we have derived the FP-KKR equation explicitly from the Kohn-Rostoker integral equation.² This FP-KKR theory still preserves the clear separation between the structural and potential information possessed in the MT-KKR equation. The potential information is contained in the S and C matrices, which can be easily calculated if the basis functions and potentials are expressed in angular-momentum expansions. Such expansions are desirable in a realistic calculation. The whole procedure has been tested against the exactly soluble Mathieu potential in the simple-cubic structure. Because of the openness of the structure and the high anisotropy of the potential, this potential provides a challenging model to test against any band-structure theory. Our results show that with wave

functions expanded up to $l_{\text{max}}=4$ and the potential up to $l_{\text{max}}=8$, the FP-KKR theory as described above gives excellent results for the bands in the energy range needed for solid-state applications. With this method, one should be able to deal with solids having open structures, such as semiconductors, for which MT-KKR is not suitable.

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APPENDIX: GREEN-FUNCTION EXPANSION

Here we want to show that Eq. (6) is valid when Eq. (7) is satisfied. Following Kohn and Rostoker,² we separate $G_{\mathbf{k}}$ of Eq. (5) into two parts,

$$G_{\mathbf{k}}(E; \mathbf{r}, \mathbf{r}') = g_0(\mathbf{k}, E; \mathbf{r}, \mathbf{r}') + g_1(\mathbf{k}, E; \mathbf{r}, \mathbf{r}') , \quad (\text{A1})$$

where g_0 is the singular part,

$$g_0(\mathbf{k}, E; \mathbf{r}, \mathbf{r}') = -\frac{1}{4\pi} \frac{\exp(i\kappa|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|} , \quad (\text{A2})$$

and

$$g_1(\mathbf{k}, E; \mathbf{r}, \mathbf{r}') = -\frac{1}{4\pi} \sum_{s \neq 0} \frac{\exp(i\kappa|\mathbf{r}-\mathbf{r}'-\mathbf{R}_s|)}{|\mathbf{r}-\mathbf{r}'-\mathbf{R}_s|} \exp(i\mathbf{k} \cdot \mathbf{R}_s) . \quad (\text{A3})$$

For $r < r' < R_s$ and for \mathbf{r} and \mathbf{r}' inside τ , the first part has the expansion $g_0 = -i\kappa \sum_L J_L(\kappa\mathbf{r}) H_L^\dagger(\kappa\mathbf{r}')$, where $H_L^\dagger(\kappa\mathbf{r}) = J_L(\kappa\mathbf{r}) + iN_L(\kappa\mathbf{r})$. Under the same condition for \mathbf{r} and \mathbf{r}' , $|\mathbf{r}| < |\mathbf{r}' + \mathbf{R}_s|$ also holds for a Wigner-Seitz cell, so that the following expansion is valid:^{6,8}

$$\begin{aligned} \frac{\exp(i\kappa|\mathbf{r}-\mathbf{r}'-\mathbf{R}_s|)}{|\mathbf{r}-\mathbf{r}'-\mathbf{R}_s|} &= -i\kappa \sum_L J_L(\kappa\mathbf{r}) H_L^\dagger(\kappa(\mathbf{r}'+\mathbf{R}_s)) \\ &= -i\kappa \sum_L \left[\sum_{L'} J_{L'}(\kappa\mathbf{r}) \mathcal{H}_{LL'}^\dagger(\kappa\mathbf{R}_s) J_{L'}(\kappa\mathbf{r}') \right] , \end{aligned} \quad (\text{A4})$$

where

$$\mathcal{H}_{LL'}^\dagger(\kappa\mathbf{R}_s) = 4\pi \sum_{L_2} i^{(l'+l_2-l)} C_{L,L_2}^{L_2} H_{L_2}^\dagger(\kappa\mathbf{R}_s) , \quad (\text{A5})$$

where $C_{L,L_2}^{L_2}$ is given in Eq. (25). Therefore the Green function has the expansion in Eq. (6) with the structure constant given by

$$B_{LL}(\mathbf{k}, E) = -i\kappa \left[\delta_{LL} + i^{(l'-l)} \sum_{s \neq 0} \mathcal{H}_{LL}^\dagger(\kappa\mathbf{R}_s) \exp(i\mathbf{k} \cdot \mathbf{R}_s) \right] . \quad (\text{A6})$$

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