the low-wave-number electron-phonon interaction, especially in metals where the Fermi surface is well known. Second, nothing is found to indicate that the general theory of ultrasonic attenuation is not completely valid within its stated limitations. Finally, it appears that, as calculations of ultrasonic attenuation become more sophisticated, greater consideration must be given to the possibility of an anisotropic electron mean free path.

ACKNOWLEDGMENTS

Thanks are due to Dr. E. S. Bliss for much helpful advice and to S. K. Wang who measured the resistance ratios in the samples.

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†Work supported by the NSF. Based on a thesis submitted by one of us (K. C. H.) as partial fulfillment of the requirements for the Ph. D. degree in physics at Carnegie-Mellon University.

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PHYSICAL REVIEW B VOLUME 4, NUMBER 4 15 AUGUST 1971

Electronic States as Linear Combinations of Muffin-Tin Orbitals

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(Received 11 January 1971)

A general method for the calculation of electronic states in solids and molecules is proposed. As in the augmented-plane-wave scheme, we use the variational principle for the Hamiltonian in an energy-dependent basis. The basis functions, so-called muffin-tin orbitals, are generalizations of Heine's resonant orbitals. For a muffin-tin potential, the secular matrix has form $(1+\Lambda U)\Lambda$, where Λ is the matrix of the Korringa-Kohn-Rostoker (KKR) method and U is a simple matrix element of the potential. In contrast to the KKr scheme, the present method easily includes perturbations to the muffin-tin Hamiltonian.

I. INTRODUCTION

The scattered-wave—or Korringa, Kohn, Rostoker (KKR)—method has proved very useful for the calculation of electronic energy levels in solids[1] and molecules,[2] whenever the muffin-tin (MT) model is appropriate; that is, whenever the one-electron potential is spherically symmetrical inside nonintersecting atomic spheres and zero outside. For low energies and short-range potentials, the secular matrix is very small, since only partial waves $\psi_{lm}(E, \vec{r})$ of nonzero phase shift and of one energy contribute. Thus the radial quantum number n of the linear-combination-of-atomic-orbitals (LCAO) matrix does not appear, instead the KKR matrix depends implicitly on energy. Although the MT model describes the potential in close-packed metals fairly well, it is not satisfactory in more open structures, in particular not when covalency is involved. Moreover, if the range of the potential is increased, more terms in the partial-wave expansion are needed. In a recent attempt[3] to extend the KKR method to the treatment of *intersecting* MT potentials, reasonable convergence was obtained for silicon only after including all partial waves up to $l = 4$. Nevertheless, the Si wave functions would probably be fairly well described by Bloch sums of *overlapping* s and p functions only, so, in this case of two atoms per unit cell, 8 rather than 50 basis functions seem appropriate. For the treatment of crystals with more atoms per cell or molecules, a small basis per atom becomes imperative.

Another limitation of the KKR formalism stems from the application of the variational principle to a functional Λ, which is not the expectation value of the Hamiltonian. Therefore, there is no simple prescription for including perturbations in the first step of a KKR calculation.

In the present paper we suggest how these inconveniences may be removed by generalizing Heine's idea on the use of resonant orbitals in an LCAO-like approach. We are not particularly interested in resonance, and the "muffin-tin orbitals" (MTO's), as previously introduced,[4] are essentially the wave functions at energy E of a single MT potential. The cores behave like atomic orbitals and—for positive energies—the tails are like plane waves. Thus, an MTO possesses both itinerant and localized behavior in proportions governed by the energy derivative of the corresponding phase shift. We shall make no attempt to separate these two properties. It was previously shown[4] that the KKR wave function may be interpreted as a linear combination of MTO's (LCMTO), and in the present paper we emphasize that the more familiar spherical-wave representation is just the one-center expansion of the LCMTO. Therefore, away from the nuclei, the LCMTO has far better l convergence than the spherical-wave expansion.

In the MTO representation, we find the MT Hamiltonian minus the energy $\langle H_{\mathrm{MT}} - E\rangle$ to be of the form $(\Lambda + \Lambda U \Lambda)$, where Λ is the KKR matrix, and the second term is the tail-tail of three-center contribution. Heine[5] anticipated the latter to be negligible for a narrow resonance, but—as we show by application to Cu and diamond—for wide bands it improves the convergence over that of the KKR method. Since Λ is a factor of the MTO matrix, the fully converged energies and wave functions are identical for the two methods. Although only complete for a MT model we feel that the MTO basis is sufficiently realistic for treating a variety of perturbations. As an example, we formulate the MTO matrix for a non-MT potential and expect to publish applications hereof to semiconductors and molecules in the near future. Finally, we mention that the use of an energy-dependent basis may cause "false zeros" of the secular determinant, and we show how they may be identified. In the MT model, false zeros can arise from the factor $(1 + U\Lambda)$.

II. MUFFIN-TIN ORBITALS

Let $\phi_{lm}(E, \vec{r})$ be that solution of Schrödinger's equation for a single MT potential which is regular at the origin and has energy E relative to the MT zero. For positive energies, ϕ is unbound but δ function normalizable; for negative energies ϕ can only be normalized at the eigenvalues. We define the MTO in such a way that it may be normalized also at negative energies outside the eigenvalues, so the formation of LCMTO's or Bloch sums causes no overlap catastrophe in general. Therefore,

$$\chi_{lm}(E, \vec{r}) = \phi_{lm}(E, \vec{r}) + c_l(E) J_{lm}(E, \vec{r}) \;, \tag{1}$$

which, outside the MT, equals

$$- s_l(E) K_{lm}(E, \vec{r}) \;. \tag{2}$$

Here, J and K are wave-equation solutions, regular at the origin and at infinity, respectively, and both are regular at zero energy. They are products of the spherical harmonic $i^l Y_{lm}(r)$ and the real radial functions

$$J_l = \kappa^{-l} j_l(\kappa r) \tag{3}$$

and

$$K_l = \kappa^{l+1} \begin{cases} i j_l(\kappa r) - n_l(\kappa r) & \text{for } E \le 0 \\ - n_l(\kappa r) & \text{for } 0 \le E \end{cases} \tag{4}$$

written in terms of spherical Bessel and Neumann functions.[6] According to whether the energy is negative or positive κ equals $i(-E)^{1/2}$ or $E^{1/2}$. Continuity of logarithmic derivatives at the MT sphere $r = S$ requires

$$s = S^2 \left[J \left(\frac{\partial}{\partial r}\right) \phi - \phi \left(\frac{\partial}{\partial r}\right) J \right]_{r=S} \;, \tag{5}$$

and c follows from continuity at the sphere. In terms of phase shifts, c/s equals $\kappa^{2l+1}(\cot\eta - i)$ and $\kappa^{2l+1}\cot\eta$ for negative and positive energies, respectively. Since MTO's at different centers are not orthogonal, and since we shall make no explicit use of the overlap matrix, the normalization has been specified by $\phi(S)$ rather than by $\int |\chi|^2 dv$. Heine's normalization[5] has not been adopted, as it is only appropriate near resonance. At eigenvalues or at resonances, c is zero, and the MTO equals the bound or resonant state ϕ. When s is zero, the MTO is confined to within the MT sphere. According to the scattered-wave terminology of Johnson,[7] cJ is the incoming and $-s\kappa$ the outgoing wave. The definition of the MTO is arbitrary within terms of J for positive energies, and here we might have defined χ equal to ϕ as was done by Heine.[5] For crystals this is illustrated by the fact that Bloch sums[8] $\sum e^{i\vec{k}\cdot\vec{R}}\chi_{lm}(E,\vec{r}-\vec{R})$ of χ's and ϕ's are equal—except at the free-electron parabola, where an overlap catastrophe occurs—because the Fourier transform of J is proportional to $\delta(k^2-E)$.

For MT's centered at points $\vec{Q}$ an LCMTO is

$$\psi(E,\vec{r})=\sum_1 A_1(E)\chi_1(E,\vec{r}-\vec{Q}) , \qquad (6)$$

writing (1) for (Qlm). The self-consistency condition for multiple scattering between nonintersecting MT's, i.e., the KKR condition, is, then, that inside the MT at $\vec{Q}$ the term $c_l J_{lm}$ of the corresponding MTO must be canceled by the tails from all other MT's. For positive energies and in terms of ϕ's, the condition is just that inside each MT the tails from all other MT's interfere destructively.[4]

III. TRANSFER OR KKR MATRIX

In order to express the LCMTO of Eq. (6) as a partial-wave expansion, we make use of an addition theorem for the tails:

$$K_L(\vec{r}-\vec{Q})=\sum_{L'L''}4\pi C_{LL'L''}\kappa^{l+l'-l''}J_{L'}(\vec{r})K^*_{L''}(\vec{Q}) , \qquad (7)$$

which holds for $r<Q$.[4] Here C is the Gaunt coefficient $\int Y_L Y^*_{L'} Y_{L''}d\hat{r}$,[9] and we have written (L) for (lm) and have suppressed the energy dependence in all functions. The addition theorem may be derived from the well-known special case[6] for the monopole field K_0 by expressing multipoles as superpositions of monopoles on a surrounding sphere. Further, Eq. (7) is a special case of Löwdin's α expansion,[10] and also a similar—but less explicit—expansion has been used by Eyges in a related paper.[11]

The transfer matrix, giving the coefficient to $J_{L'}(\vec{r}-\vec{Q}')$ in the expansion of $\chi_{QL}(\vec{r}-\vec{Q})$, is

$$T_{Q'L';QL}=c_{QL}\delta_{QQ'}\delta_{LL'}-s_{QL}(1-\delta_{QQ'})\times\sum_{L''}4\pi C_{LL'L''}\kappa^{l+l'-l''}K^*_{L''}(\vec{Q}-\vec{Q}') , \qquad (8a)$$

and for a crystal with lattice translations $\vec{R}$ and atoms at points $\vec{q}$ in the unit cell, summation over MTO's related by translation symmetry yields

$$T^k_{q'L';qL}=c_{qL}\delta_{qq'}\delta_{LL'}-s_{qL}\sum_{L''}4\pi C_{LL'L''}\kappa^{l+l'-l''}\times\sum_R(1-\delta_{q'-q,R})e^{i\vec{k}\cdot\vec{R}}K^*_{L''}(\vec{q}-\vec{q}'+\vec{R}). \qquad (8b)$$

Apart from factors which we have included to reduce the energy dependence, the KKR matrix $\Lambda_{1;2}$ of Ref. 7 equals $T_{1;2}s_2^{-1}$, and apart from a factor $S_{ql}{}^2 S_{q2}{}^2$, the KKR matrix $\Lambda^k_{1;2}$ of Ref. 12, Eq. (2.12), equals $s_1 T^k_{1;2}$. This equality may be seen by comparison with Eq. (A2.12) of Ref. 13 and by using the above-mentioned property of Bloch sums of J functions. In the following we use the latter definition of Λ—also for molecules; it may be remarked that Λ is Hermitian whereas $T^\dagger_{1;2}=s_1 T_{1;2}s_2^{-1}$.

The partial-wave expansion of an LCMTO around $\vec{Q}_1$ is

$$\psi(\vec{r})=\sum_{L_1}\psi_1(\vec{r}-\vec{Q}_1) , \qquad (9)$$

where

$$\psi_1(\vec{r}_1)=A_1\phi_1(\vec{r}_1)+[\sum_2 T_{1;2}A_2]J_1(\vec{r}_1) . \qquad (10)$$

Here $\vec{r}_1=r-\vec{Q}_1$, and this one-center expansion is valid inside the MT at $\vec{Q}_1$ and in the interstitial region inside a sphere passing through the nearest-neighbor center.[4] In Eq. (9) we have omitted the energy and for crystals the Bloch vector.

The cancellation—or KKR—condition now states that for a solution of Schrödinger's equation for a MT potential, the vector in the square bracket of Eq. (10) must vanish. As is evident from the above-mentioned equivalence between T and Λ, this condition yields the KKR eigenvalues E and eigenvectors A in the standard way, and we have thus established that the KKR eigenvector is the coefficient of both partial-wave and MTO representations, as given by Eqs. (9) and (6), respectively.

There is, however, a difference in convergence. The MTO expansion is converged when, for $l>l(\mathrm{MTO})$, $\phi(\vec{r})$ is proportional to $J(\vec{r})$, since then all phase shifts and MTO's vanish. At this point also the KKR *energies* are converged since T is diagonal for $l>l(\mathrm{MTO})$. But the partial-wave expansion is not necessarily converged, especially in the outer parts of the atomic cell. If in Eq. (7), $\max(L')=l(\mathrm{MTO})$, a radius of reasonable convergence is $[l(\mathrm{MTO})-2]/\kappa$, and at larger distances terms in the partial-wave expansion (9) with $l_1>l(\mathrm{MTO})$ contribute. Since the first term on the right-hand side of Eq. (10) together with the diagonal contribution of the second term is just the MTO at $\vec{Q}_1$, which vanishes for $l_1>(\mathrm{MTO})$, the higher partial waves are

$$\psi_1(\vec{r}_1)=[\sum_2 T_{1;2}A_2]J_1(\vec{r}_1) . \qquad (11)$$

Exactly the same result would have been obtained from the cancellation condition by requiring TA to vanish also for $l_1>l(\mathrm{MTO})$.

We therefore prefer the basis of MTO's over the partial waves for the representation of more general Hamiltonians.

IV. MTO MATRIX

A. Muffin-Tin Hamiltonian

For the MT potential $\sum_Q V_Q(|\vec{r}-\vec{Q}|)$ we find by definitions of the MTO and the transfer matrix that

$$(H_{\mathrm{MT}}-E)\chi_2(\vec{r}_2)=\sum_1 V_{Q1}(r_1)J_1(\vec{r}_1)\,T_{1;2}\ . \tag{12}$$

Since the one-center integral $(\phi_{QL}|V_Q|J_L)$ equals s_{QL} [14] the KKR matrix is

$$\Lambda_{1;2}=\int\phi_1^*(\vec{r}_1)(H_{\mathrm{MT}}-E)\chi_2(\vec{r}_2)d^3r_1\ . \tag{13}$$

The integrals only extend over the MT at $\vec{Q}_1$, and Λ therefore only includes one- and two-center terms. Equation (13) is equivalent to the original definition of Λ in Eq. (2.24) of Ref. 13. The full MTO matrix is, however,

$$\langle\chi_1(\vec{r}_1)|H_{\mathrm{MT}}-E|\chi_2(\vec{r}_2)\rangle$$

$$=\sum_3[\delta_{1;3}s_3+T^\dagger_{1;3}(J_{L_3}|V_{Q_3}|J_{L_3})]\,T_{3;2}\ , \tag{14a}$$

where as above (1) is short for $(Q_1l_1m_1)$. For Bloch sums the result is

$$N^{-1}\langle\chi_1^k(\vec{r}_1)|H_{\mathrm{MT}}-E|\chi_2^k(r_2)\rangle$$

$$=\sum_3[\delta_{1;3}s_3+T^k_{1;3}(J_{L_3}|V_{q_3}|J_{L_3})]\,T^k_{3;2}\ , \tag{14b}$$

where 1 is short for $(q_1l_1m_1)$ and N is the number of unit cells.

Thus, the MTO matrix for a MT Hamiltonian is the KKR matrix Λ plus a product $\Lambda U\Lambda$, and these may, in terms of ϕ functions, be interpreted as two- and three-center contributions, respectively.[15] Since Λ is a factor of the MTO matrix, the latter yields the same energies as the KKR method, provided that the determinant factorizes also, i.e., that T of Eq. (14) is square rather than rectangular. Now, it is implied that the internal L_3 summation is carried to convergence, and therefore only fully converged KKR energies equal fully converged MTO energies; but, the rate of convergence is expected to be faster for the latter, since in the MTO method the stationary functional *is* the energy. This is illustrated by application to C (diamond)[16] and Cu [17] in Table I. For C, where the $l=2$ phase shift nearly vanishes, the energies are reasonably converged with $\max(l)=1$ and 2, corresponding to matrix sizes for general Bloch vectors of (8×8) and (18×18) for MTO and KKR, respectively. For Cu the d phase shift resonates and the convergence of the two methods is the same. At energies above the Cu d band, the situation is as for C. For crystals with only a few atoms per unit cell, the advantage of the improved convergence may be reduced by the fact that the structure constants of Eq. (8b), which involve the elaborate lattice summations, must be calculated for all $L''\le\max(L_1)+\max(L_3)$, which may exceed the KKR value of $2\max(L_1)$. For C we used $\max(L_3)=4$, and therefore $\max(L'')=5$ and 4 for MTO and KKR, respectively. However, for solids with more atoms per cell[18] and for molecules, where large secular matrices rather than lattice summations are time consuming, the faster convergence of the MTO energies may prove useful.

B. Non-Muffin-Tin Hamiltonian

The major virtue of the MTO method is in its treatment of perturbations. The prescription is simple, and the basis functions behave reasonably throughout real space. As a simple example, we treat the one-electron potential $\sum_Q V_Q(\vec{r}-\vec{Q})$, where the individual V_Q's may be nonspherical and overlapping, but they must vanish inside all other MT's and outside a sphere through the center of the nearest neighbor. A nonoverlapping potential of this type may for instance be constructed from superposed atomic potentials by expanding in spher-

TABLE I. Comparison between KKR and MTO eigenvalues for copper and diamond with Chodorow's (Ref. 17) and Keown's (Ref. 16) MT potentials, respectively.

	Cu			C			
	KKR	MTO		KKR		MTO	
	max(l) = 2	max(l) = 2		max(l) = 1	max(l) = 2	max(l) = 1	max(l) = 2
Γ_1	−0.100	−0.100	Γ_1	−0.921	−0.921	−0.923	−0.923
Γ'_{25}	0.293	0.293	Γ'_{25}	0.557	0.512	0.522	0.510
Γ_{12}	0.354	0.354	Γ_{15}	0.968	0.907	0.917	0.901
X_1	0.156	0.156	Γ'_2	1.353	1.353	1.325	1.325
X_3	0.192	0.192	X_1	−0.318	−0.331	−0.330	−0.333
X_2	0.396	0.396	X_4	0.136	0.131	0.129	0.127
X_5	0.412	0.412	X_1	1.082	0.945	1.016	0.941
X'_4	0.718	0.708					
X_1	1.104	1.103					

ical harmonics around each nucleus, using the Löwdin expansion[10] or Eq. (7). Subsequently the expansion must be projected on the interior of the atomic Wigner-Seitz cell.[19]

Defining $\Delta V = V - V_{\mathrm{MT}}$, i.e., ΔV is the nonspherical term inside the MT and the full potential outside, we find

$$
\begin{aligned}
\langle \chi_1(\vec{r}_1) | H - E | \chi_2(\vec{r}_2) \rangle
&= \tfrac{1}{2} \textstyle\sum_3 [\delta_{1;3} S_3 + 2\delta_{Q_1;Q_3} (\phi_1 | \Delta V_{Q_1} | J_3) \\
&\quad + \textstyle\sum_4 T^{\dagger}_{1;4} \delta_{Q_3 Q_4} (J_4 | V_{Q_3} | J_3)] \\
&\quad \times T_{3;2} + \tfrac{1}{2} \delta_{Q_1;Q_2} (\phi_1 | \Delta V_{Q_1} | \phi_2) + \mathrm{H.\,c.} \qquad (15)
\end{aligned}
$$

With $\Delta V(\vec{r})$ expanded in spherical harmonics, and by use of the Gaunt coefficients, the one-center integrals reduce to radial integrals. These integrals depend only weakly on energy, except near resonance, and for small radii, J is independent of energy.

We may remark that the MTO's χ_{lm} may be generalized to χ_{lpj} by allowing the defining potential to be anisotropic inside the MT, and then including a possible coupling between different m's for the *same* l in the radial Schrödinger equation. p and j indicate for the point group of this potential, the irreducible representations and rows, respectively, so now the phase shift is η_{lp} rather than η_l. Since "radial excitations" are thus treated exactly, the "angular excitations," as caused by the l-l coupling may be treated as perturbation by means of Eq. (15), where now Y_{lm} have been coupled to Y_{lpj}, and ΔV only includes the coupling between different l's of the same (pj).

V. FALSE ZEROS

Finally a point of practical interest. Like the APW formalism,[20] the MTO formalism is much simpler, if the energy E_w of the trial wave function $\psi(E, \vec{r})$ is assumed equal to the eigenvalue E. This assumption has been made throughout the present paper, and for this reason, we did not have to evaluate the overlap matrix explicitly.

If this restriction is released, and E_w is regarded as a further variational degree of freedom, the best estimate of the true energy is the stationary value of $E(E_w)$, and for properly designed basis functions this equals E_w. However, if the stationary point is a sharp extremum, there usually exists also a nonstationary point, where $E(E_w) = E_w$, and this will appear as a "false zero" of the secular determinant. In the APW method the free-electron-like eigenvalue is almost independent of E_w, and the resonant eigenvalues exhibit sharp extrema.[21] It so happens that all $(2l+1)$ false zeros of a given resonance coincide exactly with the divergence of the logarithmic derivative, so they are not observed. The MTO method is complementary, the bound or resonant eigenvalues are flat, and the free-electron-like eigenvalues—which only occur in solids—are curved. Unfortunately, the false zero associated with the latter does not coincide with the asymptote at the free-electron parabola.

A convenient technique for identifying false zeros, which avoids calculation of the overlap matrix, consists in tracing the eigenvalues $\lambda_i(E)$, rather than the determinant $\pi_i \lambda_i(E)$, of the secular matrix, keeping E equal to E_w. The eigenvalues of the Hamiltonian are determined by $\lambda_i(E) = 0$, and a necessary—and for practical purposes sufficient—condition for $E(E_w)$ to be stationary is $\partial \lambda_i(E)/\partial E < 0$. This is easily seen from first-order perturbation theory. Although it is more complicated to calculate the eigenvalues than the determinant, our experience is that the λ technique is not more time consuming. The eigenvalues $\lambda_i(E)$ are more smooth than their product the determinant, and they may therefore be more easily interpolated. Another advantage of the λ scheme is that it yields the eigenvector of the Hamiltonian as that eigenvector of the secular matrix which has zero eigenvalue.

A λ-vs-E plot for the Cu calculation is shown in Fig. 1.

VI. CONCLUSION AND DISCUSSION

We have written the trial wave function for a one-electron state in a solid or molecule as a linear combination of muffin-tin orbitals, or

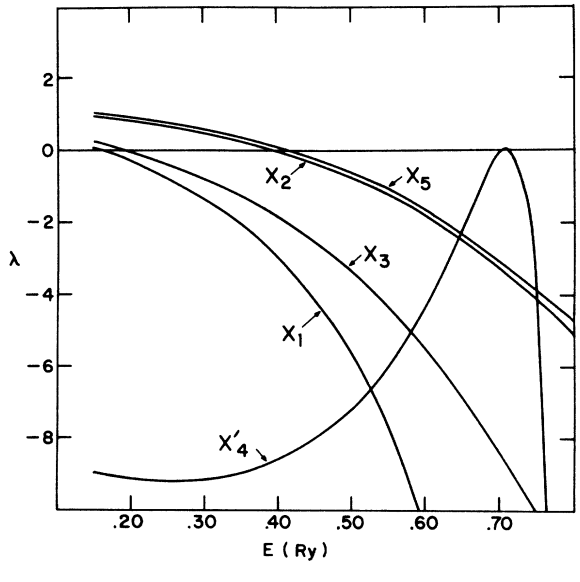

FIG. 1. λ-vs-E plot at the X point for Cu.

LCMTO [Eq. (6)]. This multicenter function has been expanded in partial waves around any single site [Eq. (9)], and the transfer matrix T [Eq. (8)], giving the single-center expansion of MTO tails, was found to be essentially the KKR matrix. So for a solution A_{Qlm} of the KKR equation, we find $TA = 0$, the tail contributions vanish, and A not only forms coefficients of this particular LCMTO, but also of its spherical wave expansion [Eq. (10)]. Moreover, this LCMTO is the wave function of the MT Hamiltonian correspondent to the MTO's.

The same solution may be obtained from the MTO equations: $\langle H_{\mathrm{MT}} - E\rangle A = 0$, where the Hamiltonian minus the energy has been written in the MTO representation [Eq. (14)]. These equations usually have better convergence than the KKR equations.

Since the MTO vanishes when the corresponding phase shift plus the phase shifts of all higher angular momenta are zero, the LCMTO is converged at this point. But the partial-wave expansion—having a radial part which is essentially a power expansion in the radius—is only converged close to the nuclei where the MT potential is strong. Therefore the basis of MTO's centered at the various sites is more suitable for the representation of perturbations to the MT Hamiltonian than is the single-center partial-wave expansion. In addition, this provides a general and simple prescription for the inclusion of perturbations in a KKR-like scheme.

We have given an expression [Eq. (15)] for $\langle H - E\rangle$ when the Hamiltonian contains a general one-electron potential. Multicenter integrals have been performed by means of single-center expansions, and therefore rather high angular momenta ($l \sim 5$) may be needed in the internal summations, especially if the potential is not weak in the interstitial region outside the MT spheres. But other ways of performing integrations over the interstitial region may be used, for instance Fourier transforms may be more appropriate for crystals.

We believe that the MTO scheme will prove convenient compared to the few other schemes available—namely LCAO[22] AND APW[23,24]—for treating general types of bands and potentials. Also, the MTO concept may be useful in the theory of impurities, surfaces, and alloys.

ACKNOWLEDGMENTS

One of us (R. V. K) would like to express his appreciation to K. H. Johnson for the use of his computer programs and many helpful discussions concerning the KKR method. We are also indebted to A. R. Mackintosh and F. M. Mueller for useful comments.

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*Contribution No. 1783.

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