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A Combined Korringa–Kohn–Rostoker–Discrete-Variational Method for the Electronic Structure of Crystals and Molecules with General Potentials

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The recently developed discrete-variational method (DVM) for the energy-band problem has been combined with the Korringa–Kohn–Rostoker (KKR) procedure to adapt the latter to treat general one-electron crystal potentials. Orbitals obtained from a KKR calculation for the muffin-tin average of the full Bloch Hamiltonian are used as trial variational functions for treating the complete problem within the framework of the DVM. Non-muffin-tin corrections originating from all regions of the unit cell are explicitly included by diagonalization of the relevant secular matrix in this basis set. This combination of the DVM and KKR methods to a large extent achieves the main advantages of each scheme and promises to comprise an efficient procedure for calculating the electronic structure of crystal compounds. With this method there is no limitation to a single-type basis set; for some purposes, it may be useful to supplement the KKR orbitals with other trial functions. The high accuracy that is achieved allows definitive conclusions to be drawn concerning the effects of the non-muffin-tin corrections on electronic structure. Illustrative results given for an application of the method to paramagnetic nickel demonstrate this point. An extension of the method is described by which the non-muffin-tin potential and charge-density corrections can be included in the multiple-scattering approach to the electronic structure of molecules.

I. INTRODUCTION

From a growing literature it is apparent that in order to obtain a clear meaning of the energy-band model for compounds, it is necessary to retain the non-muffin-tin terms in the crystal potential and charge density. By removing the muffin-tin approximation to the "exact" one-electron self-consistent crystal potential, accurate calculations reveal the adequecy of the various contributions to the model Hamiltonian and more definitively identify the inherent shortcomings.

During the past few years, a considerable number of non-muffin-tin applications[1,2] have been made with the augmented-plane-wave (APW) method.[3] Aside from the original calculations of Ham and Segall[4] however, corresponding developments with the Korringa–Kohn–Rostoker (KKR) method[5] have been few in number and have appeared only recently.

There are two regions of the unit cell for which non-muffin-tin corrections can be made. Inside the muffin-tin spheres, the nonspherically symmetric terms can be included; in the interstitial volume, approximated with a constant potential in the muffin-tin model, there are "nonflat" corrections associated with the angular and radial averaging. In most calculations which have appeared, there is a corresponding partitioning of space in the cell with different representations of the corrective terms for each region. For example, Ham and Segall[4] utilized a perturbation approach to the three-dimensional Mathieu-potential problem which involved expanding the non-muffin-tin terms inside the spheres in lattice harmonics while using Fourier expansion for the outside corrections.

Other schemes have appeared which approach the problem differently in that the basic muffin-tin KKR equations are altered. The most complete non-muffin-tin KKR calculation appears to be that of Williams and Morgan.[6] In their generalization of the KKR method, the spherical scatterers are replaced by polyhedral cells within which the crystal potential is expanded in spherical harmonics. The energy-dependent scattering matrix $\underline{t}$ which is diagonal for scattering from spherically symmetric potentials, contains nonvanishing off-diagonal elements in this case, with correspondingly more complication to the KKR equations. In this model the potential is truncated to zero at the polyhedral cell faces; however, the truncation effects are not severe in their application to silicon. Even though computational efficiency is sacrificed in generalizing that part of the calculation associated with the scattering properties, a significant advantage is gained in this approach in that non-muffin-tin corrections are included directly in the KKR equations.

A generalization of the KKR equations to correct for the nonspherical-potential components inside the spheres has been carried out by Evans and Keller[7] using trial functions and generalized phase shifts which depend on the direction of the incident wave. Recently, John, Lehmann, and Ziesche[8] have formulated the same problem based on phase shifts defined in a representation in which the directionality dependence is removed. In each case, however, the resulting equations for nonspherical-potential scatterers are considerably more complicated than the KKR equations for the corresponding set of muffin tins since the $\underline{t}$ matrix is no longer diagonal.

Modifications to the KKR equations to include weak nonflat (interstitial) potential corrections as a perturbation expansion have been proposed by Beleznay and Lawrence[9]; however, a great advantage is lost in that the structure constants are replaced by a corresponding set of factors dependent upon the interstitial potential. Another procedure has been proposed by Keller[10] to improve the representation of the potential in the region outside the atomic spheres by introducing interstitial spheres to minimize the volume of that region. Williams and Morgan[6] have found the corrections introduced in this model using interstitial muffin tins, and those originating from the nonspherical potential inside the spheres, each remove about a third of the error obtained by using the muffin-tin model alone for silicon. They find that their polyhedral scattering model removes most of the remaining error.

Another technique closely related to the KKR method and applicable to non-muffin-tin potentials satisfying certain conditions on form and range of definition has been developed by Andersen and Kasowski.[11] Their linear-combination-of-atomic-orbitals-(LCAO)-like approach uses an energy-dependent basis constructed from solutions for an isolated single-site muffin-tin potential.

In this paper, we discuss a method for including general non-muffin-tin corrections to treatments within the usual muffin-tin KKR method without reformulating the conventional KKR equations and programs. We treat the band problem with an "exact" general crystal potential by projecting out the muffin-tin average potential, finding the corresponding solutions from a KKR calculation, and using these as primary basis-set components for an accurate linear-variational treatment of the full Hamiltonian. Of central importance to this approach is the discrete-variational method, which is applicable to a wide class of problems since its formulation involves essentially no restrictions upon the form of either the basis set or the operators that appear in the Hamiltonian.

The essence of the discrete-variational method (DVM) will be briefly reviewed and limitations of LCAO basis sets discussed in Sec. II. Section III outlines our approach of uniting the KKR scheme with the discrete-variational method. Results of application of the method to nickel are presented in Sec. IV to illustrate the fundamentals of the technique, and in Sec. V we indicate how the procedures of the combined KKR-DVM scheme can be extended to treat molecular and cluster problems. In Sec. VI the advantages of this approach are summarized.

II. VARIATIONAL APPROACH

A. Discrete-Variational Method

There are numerous linear-variational methods which can be used to treat non-muffin-tin potentials, however, there are two limiting features common to the majority of these methods. First, restrictions upon the type of basis that can be used impose bounds upon the convergence rate of the solutions, and second, the non-muffin-tin terms must generally be expanded in some particular representation, thereby limiting the operators one can consider.

The DVM[12] was proposed as an alternative scheme to avoid these limitations encountered with conventional energy-band methods for compounds. In this scheme we seek variational solutions to the full one-electron crystal Hamiltonian (in atomic units)

$$H(\vec{r}) = -\tfrac{1}{2}\nabla^2 + V(\vec{r}) \;, \qquad (1)$$

where $V(\vec{r})$ represents the non-muffin-tin potential function for an electron. In terms of some arbitrary Bloch basis set, approximate solutions appear as

$$\Psi_i(\vec{k},\vec{r}) = \sum_j \chi_j(\vec{k},\vec{r})\,C_{ji}(\vec{k}) \;. \qquad (2)$$

In the DVM, the matrix elements, which reduce to integrals over a single unit cell, are evaluated directly by sampling with point density $\omega^{-1}(\vec{r})$ over M points in the unit cell, i.e.,

$$\langle \chi_i | H | \chi_j \rangle = \sum_{m=1}^{M} \omega(\vec{r}_m)\,\chi_i^*(\vec{k},\vec{r}_m)\,[H(\vec{r})\chi_j(\vec{k},\vec{r})]_m \;. \qquad (3)$$

Since we require only the numerical values of the factors in Eq. (3) over a discrete set of integration points, the restrictions on the form of the basis functions and the operators are clearly quite minor. In several applications of the DVM with Bloch LCAO basis sets,[13,14] evaluation of the one-electron matrix elements poses no problem; however, the LCAO approach itself suffers from limitations associated with convergence rates and completeness of the basis.[14]

B. Convergence Problems with LCAO Basis Sets

Characteristic of linear-variational treatments, LCAO expansions generally show rapid convergence of the valence-band structure, but the unoccupied higher-energy bands stabilize slowly.[14] The problem is in part a consequence of the fact that the LCAO basis is constructed entirely of Bloch sums of localized functions, which are not very well suited to describe the more free-electron-like solutions.[15] Conditions for rapid convergence with a fixed basis set require flexibility of the trial functions to adequately describe (preferably with a single-type function) (a) wave-function character for *all* regions of the crystal, i.e., plane-wave-like in regions where the potential is smooth and rapidly varying near the nuclei of atoms in the unit cell and (b) excited-state behavior in the high-energy region where the eigenvalues lie in the atomic continuum. It is difficult to incorporate these characteristics in a basis of manageable size derived from a set of localized functions.

The use of excited atomic orbitals of higher energy to systematically extend the basis in the LCAO approach was found to offer little increase in variational freedom in Parmenter's study of lithium.[16] For compounds, this approach has proved more useful, but experience shows that the basis problem becomes increasingly severe as we examine higher-energy regions. Although the LCAO method can be used with Bloch trial functions formed from local orbitals other than atomiclike functions,[17] there is no indication that convergence will be improved for these higher conduction bands. In any case, convergence characteristics for such basis sets can only be determined by repeated and somewhat inconclusive testing procedures.

On the other hand, in the KKR method arbitrarily exact solutions to the model Hamiltonian can be obtained, and convergence is straightforwardly controlled through the partial-wave summation. Thus, as far as completeness of the basis is concerned, the muffin-tin methods offer the advantage over fixed-basis variational approaches in that convergence can be rapidly obtained in an unambiguous way. The calculation of the excited states is carried out very efficiently in the muffin-tin model, since the centrosymmetric potential yields a radial Schrödinger equation which can be rapidly integrated for any assumed energy.

The muffin-tin solutions naturally meet all the requirements for optimizing a fixed basis for a rapidly convergent expansion of eigenfunctions of the full Hamiltonian, since they directly relate (through the muffin-tin approximate Hamiltonian) to the full Hamiltonian. Since the DVM is formulated for general basis functions, we can use the KKR solutions directly to treat the full Hamiltonian and thus achieve improved usage of each scheme—one to alleviate the basis problem, the other to remove the restrictions of the muffin-tin model.

III. COMBINED KKR-DISCRETE-VARIATIONAL METHOD

To illustrate the basic method, we consider a crystal with one atom per unit cell. To generate the basis, we partition our full one-electron Hamiltonian into a muffin-tin part $H^0(\vec{r})$ and the non-muffin-tin corrective terms $\Delta(\vec{r})$:

$$H(\vec{r}) = H^0(\vec{r}) + \Delta(\vec{r}) , \tag{4}$$

where $H^0(\vec{r}) = -\frac{1}{2}\nabla^2 + V_0(r)$. The term $V_0(r)$ is the muffin-tin average of the full potential $V(\vec{r})$, and $\Delta(\vec{r})$ contains the remaining non-muffin-tin terms.

Inside the muffin tin, the radial solutions $u_l(r)$ are efficiently obtained by integration of the radial Schrödinger equation. The solution in the region of constant potential can be expressed by scattering theoryas combinations of spherical Bessel and Neumann functions satisfying the proper boundary conditions. Explicitly, the KKR muffin-tin solution can be written[18,19] in the angular momentum representation as

$$\chi^0(\vec{k}, \vec{r}) = \sum_{l,m} i^l C_{lm}(\vec{k}) f_{lm}(\vec{r}) , \tag{5}$$

where $f_{lm}(\vec{r})$ is given by

$$f_{lm}(\vec{r}) = Y_{lm}(\Omega) \times \begin{cases} u_l(r), & r \le R_{\mathrm{MT}} \\ N_l[j_l(\alpha r) - \tan\eta_l n_l(\alpha r)], & r > R_{\mathrm{MT}} . \end{cases} \tag{6}$$

Here $j_l(\alpha r)$ and $n_l(\alpha r)$ are the Bessel and Neumann functions, respectively, η_l is the energy-dependent phase shift, and

$$\alpha = \begin{cases} i(-E)^{1/2}, & E < 0 \\ E^{1/2}, & E > 0 . \end{cases}$$

The factor N_l is given by

$$N_l = \alpha R_{\mathrm{MT}}^2 \left(u_l \frac{dn_l}{dr} - \frac{du_l}{dr} n_l \right)_{R_{\mathrm{TM}}} , \tag{7}$$

where the subscript denotes that the functions are to be evaluated at the muffin-tin radius, R_{MT}.

To illustrate the energy and spatial dependence of the scattering orbital variational basis, in Fig. 1 we plot two muffin-tin Bloch orbitals obtained from a KKR calculation for rubidium. The Γ_1 symmetry orbital derives from the rubidium 5*s* atomic state and shows rapid oscillatory behavior inside the atomic sphere. These oscillations yield rigorous orthogonality to the core orbitals of the crystal. The high-energy $\Gamma_{25'}$ orbital is the second conduction-band state of that symmetry and shows the nodal structure characteristic of a 5*d* atomic state. For several wave vectors in the Brillouin zone it was directly verified that the KKR wave-function expansion of Eq. (5) satisfies the Bloch boundary conditions at points on the unit-cell faces. While the partial-wave summation to a maximum value of 4 does not prove very time consuming for obtaining well-converged solutions, in practice a plane-wave representation for points near the cell boundary may be advantageous.[18]

In the combined KKR-DVM approach, the approximate solutions of the full Hamiltonian are expressed as linear combinations of the KKR solutions of the muffin-tin Hamiltonian:

$$\Psi_i(\vec{k},\vec{r}) = \sum_j \chi_j^0(\vec{k},\vec{r}) C_{ji}(\vec{k}) \ . \tag{8}$$

In the basis, the muffin-tin Hamiltonian H^0 is diagonal; thus at a given wave vector we only need to calculate the matrix elements of Δ, using the integration procedures employed in the DVM. Corresponding to Eq. (3), we have

$$H_{ij} = H_{ij}^0 + \Delta_{ij} = E_j^0 \delta_{ij} + \Delta_{ij} \ . \tag{9}$$

Since this operator Δ is totally symmetric under all space-group operations, only orbitals of the same symmetry subspecies can couple through the perturbation. The magnitude of the off-diagonal matrix elements of Δ provides a direct measure of the state coupling introduced through the non-muffin-tin terms. If there are no functions of like symmetry in the energy range of interest, as commonly occurs at high-symmetry points in the Brillouin zone for metals, the energy shifts are the same as the first-order perturbation corrections. In compounds, however, there are typically closely spaced levels of the same symmetry at a general wave vector, and the solutions corresponding to the full Hamiltonian will be obtained as linear combinations of these KKR orbitals when the matrix Δ is diagonalized.

Since the basis functions are rigorously orthogonal among themselves and to the core orbitals, there is no core orthogonality problem and the states of interest for the calculation of physical properties can be considered without explicitly including the inner-core functions. The possible coupling of the higher-energy core functions to the states of interest is easily handled, but generally is not expected to be sufficiently strong to enter the secular problem. Although Δ is often of crucial significance within the muffin-tin spheres, it becomes vanishingly small in the inner-core region and can thus institute only negligible coupling between the valence and the deeper-core states. Thus secular matrices can be kept to small size—an important requirement for treating compounds of the heavy elements.

There is no necessity in this method to form analytic representations of the potential, thus quite general one-electron potentials can be treated. Formation of the matrix Δ involves simply a point sampling of $\Delta(\vec{r}) = V(\vec{r}) - V_0(\vec{r})$ over the unit cell, and the particular representation of $V(\vec{r})$ or $V_0(\vec{r})$ is of no consequence–in practice both $V(\vec{r})$ and $V_0(\vec{r})$ are used in numeric form in our calculations.

The main way in which our proposed scheme differs from the techniques based on reformulations

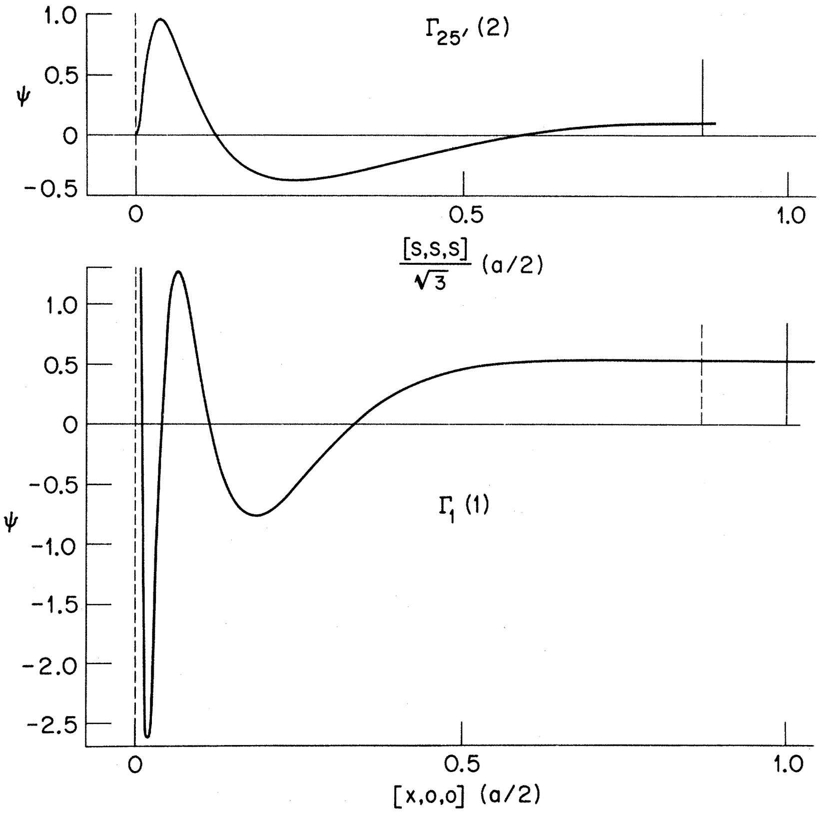

FIG. 1. Trial KKR wave functions (unnormalized) at the symmetry point Γ in rubidium (lattice constant $a = 10.74$ a.u.). The $\Gamma_1(1)$ orbital in the lower part of the figure is an occupied state at an energy of -0.212 a.u.; the $\Gamma_{25'}(2)$ is the second conduction-band level of that symmetry and lies as 0.322 a.u. The solid vertical lines crossed by the orbitals represent the Wigner–Seitz cell faces, while the broken vertical line designates the muffin-tin radius. The Rb nucleus is at the origin of the horizontal scale.

TABLE I. Energy eigenvalues E_i of high-symmetry levels for Ni including non-muffin-tin terms with corresponding level shifts from those in the muffin-tin approximation E_i^0; $W-W^0$ denotes changes in energy-band separations and widths upon including non-muffin-tin corrections to the potential (energies in rydbergs).

Level	E_i	$E_i-E_i^0$	$W-W^0$	
Γ_1	-1.117	0.003		
Γ_{12}	-0.523	0.002	s-d separation	
$\Gamma_{25'}$	-0.602	-0.000	$\Gamma_{25'}-\Gamma_1$	-0.003
X_1	-0.785	0.010		
X_5	-0.452	0.000	$X_5-\Gamma_1$	-0.004
			d width	
			X_5-X_1	-0.010
$X_{4'}$	-0.284	-0.009	s-p width	
			$X_{4'}-\Gamma_1$	-0.013
X_2	-0.469	0.001		
X_3	-0.739	-0.003		
$L_{2'}$	-0.488	0.010		
$L_1(1)$	-0.792	-0.004		
$L_1(2)$	-0.013	-0.002		
$L_3(1)$	-0.607	0.000		
$L_3(2)$	-0.467	0.000		

or modifications of the muffin-tin KKR equations is that conventional KKR and DVM procedures are maintained in the combined KKR-DVM scheme. Our goal is to maintain the most efficient computational mode of the KKR in order to utilize to the maximum extent the efficient mathematical techniques applicable to the muffin-tin model. When we have exhausted that model completely, then we include non-muffin-tin terms by resort to the variational treatment.

In the KKR-DVM approach, corrections to the band structure enter first from shifts which are first order in origin and second from off-diagonal couplings of the Bloch basis states through the non-muffin-tin potential. The major question at present involves how well the admixture of muffin-tin eigenstates represents the true solution, and whether it will be necessary to supplement the Bloch muffin-tin solutions with other trial functions.

IV. APPLICATION TO PARAMAGNETIC NICKEL

The combined KKR-DVM technique has been developed primarily to treat crystalline compounds; however, initial usage has been restricted to a few metallic crystals for which recent KKR energy-band results are available. Preliminary calculations of the non-muffin-tin energy corrections for lithium were found to agree well with available LCAO[12] and non-muffin-tin APW[1] results. For illustrative purposes in this paper, we report some results of calculations for the paramagnetic form of fcc nickel. Our purpose here is simply to calculate the effects of the anisotropic potential within a limited paramagnetic band model. More thorough investigations of nickel are reported in the literature.[20] Because of the small effects in metals, the calculation forms a stringent test of the accuracy of the KKR-DVM; the accuracy is found sufficient that we can make definitive statements about the effects of the non-muffin-tin potential and charge density on the band structure and total energies of metals.

In Table I we summarize the non-muffin-tin energy shifts from the KKR muffin-tin eigenvalues E_i^0 calculated at several symmetry points in the Brillouin zone. The corrected eigenvalues E_i result from the combined KKR-DVM treatment of the full Hamiltonian; i.e., the operator $\Delta(\vec{r})$ in this case is given by

$$\Delta(\vec{r}) = V(\vec{r}) - V_0(\vec{r}) , \qquad (10)$$

where $V(\vec{r})$ is the full crystal potential obtained from directly superimposing atomic potentials and charge densities using the free-atom charge density appropriate to a $3d^{9.4}4s^{0.6}$ valence-shell configuration as calculated in the Herman–Skillman[21] atomic program and $V_0(r)$ is the corresponding muffin-tin average. The KKR wave functions used in this preliminary work were obtained in symmetrized form with an upper limit in the partial-wave sum of 4. An integration mesh of 2400 points in the DVM stage converges the eigenvalues to at least three significant figures for the energy range considered in Table I.

Generally, the effect of the anisotropic corrections is a narrowing of bandwidths and energy separations. Practically all of the energy shifts in this energy range of about 1.0 Ry are first order, the allowed coupling of the states at the L point contributing energy differences an order of magnitude smaller than the first-order shifts alone. Calculations performed in the often used "warped-muffin-tin" approximation, obtained by truncating Δ within the muffin-tin sphere, indicate that more than 80% of the total energy shift results from non-muffin-tin corrections outside the spheres. Coupling of the core $3p$ states to the valence levels is entirely negligible.

Substantial energy shifts do occur for some of the states upon which predictions of the Fermi surface depend quite sensitively. The d-band width is reduced by 0.010 Ry in good agreement with that obtained by Jacobs.[22] This reduction is of the same order of magnitude as the shifts found in Connolly's study[23] of the effects of using various muffin-tin potentials. The magnitude of this narrowing, if assumed the same for the ferromagnetic case, is not great enough to resolve the discrepancy between theoretical calculated band densities of states and x-ray-photoemission experimental data,[24] and hence provides some further information on the shortcomings of the assumed energy-band model.

The size of the hole pocket associated with the X_5 level appears unperturbed by the non-muffin-tin corrections. The $L_{2'}$ state, which is important in determining the neck in the Fermi surface at L, shifts by +0.010 Ry—this shift is an order of magnitude greater than that obtained by simpler estimation procedures.[23] The order of the states $L_{2'}$ and L_3 remains the same for this potential configuration, however. From these results, it is clear that for those properties which can be meaningfully obtained within the one-electron energy-band model, particularly Fermi-surface characteristics, the non-muffin-tin effects can be sufficiently large to affect detailed comparison with experiment and should be properly accounted for.

V. MOLECULAR CLUSTER PROBLEM

The multiple-scattering (KKR) method has been applied with considerable success in recent years to the calculation of the electronic states of molecular clusters in the muffin-tin approximation[25] using a local exchange approximation.[26] A comparative study[27] of treatments using the KKR cluster method and the usual LCAO approach for large molecules demonstrates an impressive advantage of the KKR scheme with regard to computation time. However, this computational efficiency is based on the simplicity of the assumed muffin-tin-model molecular potential. From simple geometrical considerations, one would expect the muffin-tin approximation to be inadequate in all but exceptional cases. Recent total-energy calculations for several molecules show that the partitioning and averaging effects of the cluster muffin-tin model are especially severe in the treatment of molecules having lone pair states and asymmetrical bonds.[28] As observed with similar crystal-cohesive-energy calculations,[29] the non-muffin-tin terms in the charge density appear crucial in predicting dissociation energies and bond angles.

Obviously, a combined KKR-DVM technique can be devised for the molecular case. A clear equivalence exists between the KKR approach and the LCAO scheme in a Bloch basis on one hand and the multiple-scattering cluster technique and the LCAO method in a symmetrized molecular-orbital basis on the other. In complete analogy with the procedures described for the energy-band model, the DVM and the KKR cluster method can be united to remove the restrictions of the muffin-tin-model charge density and potential, and all of the mutual advantages of the DVM and the KKR method result as previously discussed. It should then be possible to reach definitive conclusions regarding the effects of these corrections in clusters and to resolve questions concerning the sensitivity of results to the rather arbitrarily chosen muffin-tin radii. This scheme is presently being set up, and we expect to publish applications to clusters in the near future.

A more interesting prospect is that of using KKR orbitals with the DVM as adapted for two-electron integrals[30] for electronic structure and total-energy calculations within Hartree-Fock (HF) and configuration-interaction (CI) formulations wherein the two-particle interactions enter as corrective terms. Solution of a muffin-tin model of the system would yield a set of orbitals which form a quite reasonable basis set to achieve a rapidly convergent CI series.

VI. SUMMARY

The success of previous applications of the DVM has been based on its *operator* versatility which has allowed us to accurately treat the anisotropic potentials in covalent crystals. In this paper we have described an approach which uses the *basis-function* flexibility of the scheme to avoid the convergence problems encountered in the LCAO method. Within the KKR-DVM scheme, a variety of model Hamiltonians can be considered without introducing further approximations—a necessary requirement for determining the adequacy of various aspects of the theoretical models.

Our present efforts concern generalizing the KKR programs to treat complex crystals.[31] Results therefrom will provide a meaningful basis for comparison with the other recent non-muffin-tin KKR methods. From existing results, however, the combined KKR-DVM offers considerable promise for treating complex crystal compounds within more refined models.

In summary, we have presented an energy-band method which is generally applicable to any ordered crystal, although specifically intended to treat crystalline compounds. The motivating philosophy is that the mathematical simplicity inherent in the muffin-tin model should be exploited through the efficient computational procedures developed for that problem, with the treatment of the non-muffin-tin corrections reserved for less specialized but more flexible procedures (DVM). Wave functions are obtained in the muffin-tin approximation using the KKR method, and used as a trial basis for the DVM to carry out a variational treatment of the full Hamiltonian. A generalization of the technique has been described to treat similar problems in the calculation of the electronic structure of molecular clusters.

To summarize some advantages of this method, the restrictions of the muffin-tin model are completely removed without sacrificing the computational efficiency of the KKR method—no modification of existing KKR muffin-tin schemes is required. Non-muffin-tin corrections are calculated directly and on the same footing for all regions of the cell without any partitioning. Thus no perturbative formulation is used; energy corrections are calculated by directly diagonalizing the relevant secular matrix. A major advantage of the KKR method is maintained in that the secular problem for the full Hamiltonian involves matrices of small size. The KKR expansion basis comprises a convenient representation for further use and analysis of the wave functions.

The method has been illustrated by calculating the small non-muffin-tin shifts in paramagnetic nickel. In addition to demonstrating the high accuracy of the procedure, the results show that it is possible to attain definitive information concerning the influence of non-muffin-tin corrections for Fermi-surface calculations within conventional muffin-tin methods. Viewed either as the KKR corrected to include non-muffin-tin effects or as the DVM with KKR scattering orbitals as a basis, the two schemes have been combined to achieve the main advantages of each.

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