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Variational methods for cellular models

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Two complementary variational principles are derived for the one-electron Schrödinger or local-density-functional equation in a closed cell of arbitrary shape, for external Neumann and Dirichlet boundary conditions, respectively. The surface operators $\mathcal{R}$ and $\mathcal{R}^{-1}$, respectively, are stationary in these two variational principles. Subject to a condition of compatibility of the boundary conditions, these results are combined to give variational equations that are valid for an arbitrary cluster of atomic cells, assumed to fill space within an outer boundary. Cell interface terms agree with prior variational derivations for discontinuous functions. It is shown that structure constants of multiple scattering theory can be used within the variational formalism, giving contracted Hermitian matrix equations linearized in energy. New variational prescriptions are given for two broad classes of applications: (i) electron scattering by a cluster, or bound states using scattering theory; (ii) embedding a cluster in a substrate.

I. INTRODUCTION

The computation of electronic properties of complex systems, such as solids, surfaces, or large molecules, can be carried out in practice only by introducing an effective one-electron Hamiltonian, designed to model effects of exchange and correlation. The most successful and widely used method is the local-density-functional (LDF) theory of Hohenberg, Kohn, and Sham.[1] Given such a model Hamiltonian, the problem of complex geometry is still a formidable obstacle. Because methods based on space-filling local cells have traditionally been inefficient, alternative methods based on a local sphere approximation have been widely used.

A new variational principle, suitable for space-filling atomic cells, has recently been derived.[2] This formalism has been developed into a nonspherical multiple scattering method, and applied to self-consistent energy-band calculations, in particular for fcc Cu,[3] including an empty-lattice test for this lattice.[4] A linear operator $\mathcal{R}$ is defined that produces function values on the surface Σ of a closed cell Ω when acting on normal gradient values on Σ. The $\mathcal{R}$ operator is determined by variational solution of the Schrödinger equation in the interior of Ω. At specified energy ε, boundary matching to an external wave function is completely determined by $\mathcal{R}$ on surface Σ.

In typical applications, the system to be considered is a finite or infinite cluster of atoms. It is convenient and efficient to define a separate cell for each atom, and then to use variational basis functions obtained by numerical integration of the local Schrödinger (or Dirac) equation in each atomic cell. At given ε, the $\mathcal{R}$ operators for elementary cells can be concatenated to form a global $\mathcal{R}$ operator defined over the outer boundary surface of a cluster.[2] While this formalism is appropriate to such applications as electron-molecule scattering, it is more efficient for applications such as energy band calculations to extend the formalism to simultaneous calculations over a range of energies, using linearized methods. This has been done in the case of a monatomic translational cell by developing the atomic-cell-orbital (ACO) method. This is a refinement of Korringa-Kohn-Rostoker (KKR) multiple scattering theory[5] in which the spherical muffin-tin model is replaced by space-filling atomic Wigner-Seitz cells.[3] The energy-linearized version of this linearized atomic-cell-orbital (LACO) method is modeled directly on the linearized muffin-tin orbital (LMTO) method of Andersen,[6,7] in which translational boundary conditions are imposed by use of energy-independent structure constants.

For practical applications, a polyatomic translational cell or atomic cluster must be considered. In order to use ACO basis functions defined separately in each atomic cell, these functions must be matched across the interfaces between adjacent cells. $\mathcal{R}$-operator concatenation[2] at fixed ε does not take advantage of the energy linearization made possible by use of energy-independent structure constants in the LMTO and LACO methods. Two alternative strategies are used in current practice to treat the interface matching problem. The first is the use of KKR structure constants, as in the LMTO method.[6,7]

Locally defined atomic basis functions and their energy derivatives are combined to fit standard solid harmonic functions on the local cell boundary. Because the solid harmonics are continuous and have known translational properties, as characterized by the KKR structure constants, extension of muffin-tin orbital (MTO) or ACO basis functions throughout a cluster or solid is determined by fitting to the local representation of the solid harmonics.

The second strategy for matching at interfaces is to use a variational principle for functions that are discontinuous across such an interface. Such a variational principle was derived some time ago by Schlosser and Marcus.[8] An equivalent variational principle has been used more recently in the variational cellular method (VCM) of Leite and co-workers.[9–11] As used by Leite *et al.*, basis functions at specified ε define an Hermitian matrix of surface integrals over the interface boundaries. Linear combinations of basis functions are defined by null vectors of this matrix. The method is not linear in energy, requiring a search for zeros of a secular determinant. Nonphysical zeros occur that must be eliminated by an auxiliary condition.

The purpose of the present paper is to develop a variational formalism in which the relationship between the $\mathcal{R}$-operator variational principle[2] and the principle of Schlosser and Marcus[8] or VCM (Ref. 9) will be clear. Within this general formalism, practical methods will be proposed that exploit the complementary advantages of energy-independent structure constants and of variational boundary terms in an extended Hamiltonian matrix.

The variational principle for the $\mathcal{R}$ operator is summarized and rederived in Sec. II here, and an analogous principle for the $\mathcal{R}^{-1}$ operator is derived. These derivations make use of Neumann and Dirichlet boundary conditions, respectively. If the externally imposed function values or normal gradients on surface Σ satisfy a consistency condition, the two distinct variational equations can be combined. The resulting matrix equation in a given variational basis contains only Hermitian operators.

Section III extends this derivation to a system described as a cluster of atomic cells. The variational equations without external boundary terms are shown to be equivalent to those derived by Schlosser and Marcus.[8] If basis functions are solutions of the local Schrödinger equation at a specified common energy ε, the variational equations reduce to the VCM equations of Leite *et al.*[9]

Section IV discusses the use of KKR structure constants in the context of the derived variational equations. Methodology is proposed appropriate to electron scattering and to the general embedding problem.

II. VARIATIONAL PRINCIPLES FOR EXTERNAL BOUNDARY CONDITIONS

The stationary principle for the $\mathcal{R}$ operator[2] is derived by considering arbitrary Neumann boundary conditions. Values of the outward normal gradient ξ are imposed on the boundary Σ of a closed volume Ω. Given the one-electron Hamiltonian h, at energy ε in Rydberg units, define the functional

$$\Xi=\int_{\Omega}\psi^{*}(h-\varepsilon)\psi\,d\tau\ . \tag{1}$$

The auxiliary functional

$$A=\Xi+\int_{\Sigma}\psi^{*}\nabla_{n}\psi\,d\Sigma \tag{2}$$

is obtained by integration by parts. A is the mean value of a Bloch-modified Hamiltonian operator.[12] Matrix elements of A, Hermitian in any representation basis, are

$$A_{ab}=\int_{\Omega}[\nabla\phi_{a}^{*}\cdot\nabla\phi_{b}+\phi_{a}^{*}(V-\varepsilon)\phi_{b}]d\tau\ , \tag{3}$$

in Rydberg atomic units. The mean value A is necessarily real. The boundary integral

$$A_{1}=\int_{\Sigma}\psi^{*}\xi\,d\Sigma \tag{4}$$

is defined by normal gradient values ξ on Σ. In Eq. (2), Ξ vanishes for an exact solution of the Schrödinger equation in Ω. Hence if $\nabla_{n}\psi=\xi$ on Σ for such a solution

$$A=A_{1}=A_{1}^{*}\ . \tag{5}$$

Consider the variational functional

$$[A]=A_{1}A^{-1}A_{1}^{*}\ , \tag{6}$$

defined in analogy to the Schwinger variational principle of scattering theory. It follows from the defining equations that, for fixed ξ and for variations of ψ about an exact solution, $\delta[A]=0$ if and only if

$$\begin{aligned}&\text{(i)}\ \ (h-\varepsilon)\psi=0\ \ \text{in}\ \Omega\ ,\\ &\text{(ii)}\ \ \nabla_{n}\psi=\xi\ \ \text{on}\ \Sigma\ .\end{aligned} \tag{7}$$

Expand ψ as $\Sigma\phi_{a}c_{a}$ in a basis of functions $\{\phi_{a}\}$. Then the coefficients satisfy the variational equation

$$\sum_{b}A_{ab}c_{b}=\int_{\Sigma}\phi_{a}^{*}\xi\,d\Sigma\ . \tag{8}$$

This can be expressed in a compact matrix notation

$$Ac=f^{\dagger}\xi\ , \tag{9}$$

where f is a rectangular matrix in which each basis function is represented by a vector of its values at quadrature grid points on surface Σ, while ξ denotes the corresponding vector of normal gradient values, multiplied by quadrature weights at these grid points. In this notation, the stationary value of $[A]$ is

$$[A]=\xi^{\dagger}\mathcal{R}\xi\ , \tag{10}$$

where, defined as a matrix over quadrature points on Σ,

$$\mathcal{R}=fA^{-1}f^{\dagger}\ . \tag{11}$$

Since ξ is arbitrary, the stationary property of $[A]$ implies that $\mathcal{R}$ is itself stationary. Equation (11) is used to compute $\mathcal{R}$ in any linearly independent basis.

Equation (9) gives a variational solution of the classical Neumann problem for the Schrödinger equation. The $\mathcal{R}$ operator is more general than this equation, since it completely determines boundary matching conditions on surface Σ. The external wave function at specified ε must have function values η at quadrature grid points on Σ such that

$$\eta=\mathcal{R}\xi \ . \tag{12}$$

In scattering theory, the scattering matrix occurs linearly in both η and ξ and is determined by Eq. (12). Values of the variational wave function ϕc on surface Σ, determined by Eqs. (9) and (11), are

$$F=fc=\mathcal{R}\xi=\eta \ . \tag{13}$$

An analogous stationary principle for $\mathcal{R}^{-1}$ can be derived by considering arbitrary Dirichlet boundary conditions, specified by function values η on surface Σ. The appropriate functionals are

$$B=\int_{\Sigma}(\nabla_n\psi)^*\psi\, d\Sigma-\Xi \ , \tag{14}$$

and

$$B_1=\int_{\Sigma}(\nabla_n\psi)^*\eta\, d\Sigma \ . \tag{15}$$

The functional B is real, the corresponding matrix $\underline{B}_{ab}$ in any basis $\{\phi_a\}$ is Hermitian, and for exact solutions of the Schrödinger equation and Dirichlet boundary conditions

$$B=B_1=B_1^* \ . \tag{16}$$

The variational functional

$$[B]=B_1B^{-1}B_1^* \tag{17}$$

is defined so that for variations of ψ about an exact solution, for fixed η, $\delta[B]=0$ if and only if

$$\begin{aligned}&\text{(i)}\ (h-\varepsilon)\psi=0 \ \text{ in } \Omega \ ,\\ &\text{(ii)}\ \psi=\eta \ \text{ on } \Sigma \ .\end{aligned} \tag{18}$$

The variational equations are

$$Bc=g^\dagger\eta \ , \tag{19}$$

where g is the rectangular matrix of normal gradients of basis functions times quadrature weights at quadrature points on surface Σ. The stationary value of $[B]$ is

$$[B]=\eta^\dagger\mathcal{R}^{-1}\eta \ , \tag{20}$$

where, defined as a matrix over quadrature points on Σ,

$$\mathcal{R}^{-1}=gB^{-1}g^\dagger \ . \tag{21}$$

Because η is arbitrary, $\mathcal{R}^{-1}$ is stationary. It is computed from Eq. (21). The external normal gradient function on Σ at energy ε must satisfy

$$\xi=\mathcal{R}^{-1}\eta \ . \tag{22}$$

Equation (19) gives a variational solution of the classical Dirichlet problem for the Schrödinger equation. From Eqs. (19) and (21), the weighted outward normal gradient of the variational wave function is given on Σ by

$$G=gc=\mathcal{R}^{-1}\eta=\xi \tag{23}$$

from Eq. (22).

In the limit of completeness of the basis, Eqs. (9) and (19) must be compatible at given ε. Assuming Eq. (23), in this limit, Eq. (9) is equivalent to the system of homogeneous equations

$$(A-f^\dagger g)c=0 \ . \tag{24}$$

Similarly, for a complete basis, Eq. (19) is equivalent to

$$(B-g^\dagger f)c=0 \ . \tag{25}$$

From Eqs. (2) and (14), the matrix elements in Eqs. (24) and (25), respectively, are

$$\begin{aligned}(A-f^\dagger g)_{ab}&=(h-\varepsilon)_{ab} \ ,\\ (B-g^\dagger f)_{ab}&=-(h-\varepsilon)_{ab} \ .\end{aligned} \tag{26}$$

Hence, Eqs. (9) and (19) are identical in the limit of completeness of the basis.

For an arbitrary finite basis, Eqs. (9) and (19) are not in general equivalent, but they are both valid as variational approximations. It is legitimate to combine these two equations in the form

$$\tfrac{1}{2}(A-B)c=\tfrac{1}{2}(f^\dagger\xi-g^\dagger\eta) \ . \tag{27}$$

Eliminating matrix B_{ab} by use of Eqs. (26), this can be expressed in the form

$$[A-\tfrac{1}{2}(f^\dagger g+g^\dagger f)]c=\tfrac{1}{2}(f^\dagger\xi-g^\dagger\eta) \ . \tag{28}$$

It will be shown in Sec. III, below that when a cluster of atomic cells is considered, Eq. (28) is of the same form as the subset of equations for each local cell given by the Schlosser-Marcus[8] variational equations for discontinuous basis functions. Equation (28) is proposed here as the basic equation of the ACO method for clusters of cells.

If the basis functions are all eigenfunctions of $h-\varepsilon$ for specified ε, then $f^\dagger g$ and $g^\dagger f$ are equal and Hermitian by Green's theorem. From Eqs. (2) and (14) in this case,

$$A=B=f^\dagger g=g^\dagger f \ . \tag{29}$$

In such a basis, used in the VCM formalism,[10] the left-hand member of Eqs. (27) or (28) vanishes identically. Consistency requires that the right-hand member must vanish, which establishes a linear relationship between ξ and η. It can easily be shown that this relationship is equivalent to either Eq. (12) or Eq. (22) and that matrices $\mathcal{R}$ and $\mathcal{R}^{-1}$ are inverse to each other in this case.

In an arbitrary basis, chosen to span an energy range, Eqs. (29) are not valid, and the matrices in Eqs. (26) are not Hermitian. The matrix in the first member of Eq. (28) is Hermitian by construction. Imposing fixed or periodic boundary conditions on all the basis functions, the resulting homogeneous equations have vector solutions at a discrete set of energy eigenvalues ε. These energies determine the bound-state energy spectrum.[9,10] When energy ε is specified, as in scattering theory, Eq. (28) has solutions except at eigenenergies, for any given ξ and η, but ξ and η cannot be specified independently of each other. Given either one of these functions, the variational wave function is determined either by Eq. (9) or by Eq. (19). Then ξ and η are related by Eq. (12) or by Eq. (22).

III. VARIATIONAL PRINCIPLE FOR A CLUSTER OF ATOMIC CELLS

In a cluster of cells, each separate cell is governed by Eq. (28). On an interface $\Sigma_{\mathrm{I,II}}$ shared by adjacent cells Ω_{I} and Ω_{II}, boundary values ξ and η that are external to cell I can be expanded in the basis for cell II in the form

$$\eta_{\mathrm{I,II}} = f_{\mathrm{II}} c_{\mathrm{II}} \ , \tag{30}$$

$$\xi_{\mathrm{I,II}} = -g_{\mathrm{II}} c_{\mathrm{II}} \ . \tag{31}$$

By convention here, g_{II} refers to normal gradients that are outward with respect to cell II, while $\xi_{\mathrm{I,II}}$ refers to outward normal gradients with respect to cell I. This accounts for the negative sign in Eq. (31). In the notation used here, f_{II} is a rectangular matrix indexed by basis functions in cell II and by surface quadrature points on the interface $\Sigma_{\mathrm{I,II}}$, and similarly for g_{II}.

A particular cell Ω_{I} can have several adjacent cells Ω_X sharing interface surfaces $\Sigma_{\mathrm{I},X}$, leaving a residual surface $\Sigma_{\mathrm{I,ext}}$ that is a portion of the outer boundary of the cluster. Since Eq. (28) must be satisfied simultaneously for each cell in the cluster, the full set of equations to be solved are obtained by using Eqs. (30) and (31) at each interface, transferring all interface terms to the left-hand member. The resulting equations are

$$\begin{bmatrix} A_{\mathrm{I,I}} - \frac{1}{2}(f^\dagger g + g^\dagger f)_{\mathrm{I,I}} & \frac{1}{2}(f^\dagger g + g^\dagger f)_{\mathrm{I,II}} \cdots \\ \frac{1}{2}(f^\dagger g + g^\dagger f)_{\mathrm{II,I}} & A_{\mathrm{II,II}} - \frac{1}{2}(f^\dagger g + g^\dagger f)_{\mathrm{II,II}} \cdots \\ \vdots & \vdots \end{bmatrix} \begin{bmatrix} c_{\mathrm{I}} \\ c_{\mathrm{II}} \\ \vdots \end{bmatrix} = \begin{bmatrix} \frac{1}{2}(f^\dagger \xi - g^\dagger \eta)_{\mathrm{I,ext}} \\ \frac{1}{2}(f^\dagger \xi - g^\dagger \eta)_{\mathrm{II,ext}} \\ \vdots \end{bmatrix} . \tag{32}$$

The homogeneous part of Eq. (32) can be derived directly, using the variational principle of Schlosser and Marcus.[8] Consider two adjacent cells, Ω_{I} and Ω_{II}, that share an interface surface $\Sigma_{\mathrm{I,II}}$. The variational functional of Schlosser and Marcus for this case, when expanded in a fixed set of basis functions $\{\phi_{\mathrm{I}}\},\{\phi_{\mathrm{II}}\}$, can be reduced by integration by parts and is expressed in the present notation by

$$Z = (c_{\mathrm{I}}^\dagger, c_{\mathrm{II}}^\dagger) \begin{bmatrix} Z_{\mathrm{I,I}} & Z_{\mathrm{I,II}} \\ Z_{\mathrm{II,I}} & Z_{\mathrm{II,II}} \end{bmatrix} \begin{bmatrix} c_{\mathrm{I}} \\ c_{\mathrm{II}} \end{bmatrix} , \tag{33}$$

where the matrix occurring here is identical with the (I,II) submatrix in the left-hand member of Eq. (32). It is shown by Schlosser and Marcus for variations of wave functions ψ_{I} and ψ_{II} about exact solutions, satisfying continuity conditions across $\Sigma_{\mathrm{I,II}}$, that $\delta Z = 0$ if and only if

$$\begin{aligned} &\text{(i)} \ \ (h-\varepsilon)\psi = 0 \ \text{ in both } \Omega_{\mathrm{I}} \text{ and } \Omega_{\mathrm{II}} \ , \\ &\text{(ii)} \ \ \psi_{\mathrm{I}} = \psi_{\mathrm{II}} \ \text{ on } \Sigma_{\mathrm{I,II}} \ , \\ &\text{(iii)} \ \ \nabla_n \psi_{\mathrm{I}} = -\nabla_n \psi_{\mathrm{II}} \ \text{ on } \Sigma_{\mathrm{I,II}} \ . \end{aligned} \tag{34}$$

Since the matrix in Eq. (33) is Hermitian, the variational equations for the coefficient vectors $c_{\mathrm{I}}, c_{\mathrm{II}}$ are of the same form as the homogeneous part of Eq. (32). When the sign convention for the normal gradient is taken into account, the inhomogeneous term in the right-hand member of Eq. (32) is required, by compatibility with the off-diagonal blocks of the homogeneous term, to have the form given here.

If basis functions are used that are eigenfunctions of $h-\varepsilon$ at a unique given value of ε, the cell-diagonal blocks in Eq. (32) vanish because Eq. (29) is valid. The nondiagonal blocks in the left-hand member of Eq. (32) constitute an Hermitian matrix identical with the matrix used in the VCM formalism.[9] In VCM calculations of bound states, periodic boundary conditions are incorporated by modifying the homogeneous part of Eq. (32) as in Eqs. (24) or (25) here. Eigenstates are obtained by searching for null vectors of the resulting system of homogeneous linear equations.

Equation (32) generalizes the VCM formalism by retaining the cell-diagonal terms so that basis functions can be used that span a range of energies, facilitating the development of energy-linearized methods. Nontrivial external boundary conditions can be imposed through the explicit appearance of ξ_{ext} and η_{ext} in the inhomogeneous term in Eqs. (32). Consistency conditions analogous to Eqs. (9) or (19) are required to connect functions ξ_{ext} and η_{ext}. Because $\mathcal{R}$ and $\mathcal{R}^{-1}$ are Hermitian matrices, these functions must satisfy Green's theorem, in the form

$$(\eta^\dagger \xi - \xi^\dagger \eta)_{\mathrm{ext}} = 0 \ . \tag{35}$$

The correct variational equations for the $\mathcal{R}$ operator defined on the external boundary of a cluster are obtained by including the internal interface terms of the Schlosser-Marcus functional Z in the functional A of Eq. (2). The modified variational equations are

$$\begin{bmatrix} \tilde{A}_{\mathrm{I,I}} & \tilde{A}_{\mathrm{I,II}} & \cdots \\ \tilde{A}_{\mathrm{II,I}} & \tilde{A}_{\mathrm{II,II}} & \cdots \\ & \vdots & \end{bmatrix} \begin{bmatrix} c_{\mathrm{I}} \\ c_{\mathrm{II}} \\ \vdots \end{bmatrix} = \begin{bmatrix} (f^\dagger \xi)_{\mathrm{I,ext}} \\ (f^\dagger \xi)_{\mathrm{II,ext}} \\ \vdots \end{bmatrix} , \tag{36}$$

where

$$\begin{aligned} &\tilde{A}_{\mathrm{I,II}} = A_{\mathrm{I,I}} - \tfrac{1}{2}(f^\dagger g + g^\dagger f)^{\mathrm{int}}_{\mathrm{I,I}} \ , \\ &\tilde{A}_{\mathrm{I,II}} = \tfrac{1}{2}(f^\dagger g + g^\dagger f)_{\mathrm{I,II}} \ , \\ &\vdots \end{aligned} \tag{37}$$

The notation $(\ )^{\mathrm{int}}$ here refers to integrals taken over the interface portion of Σ_{I}, excluding points on the outer surface of the cluster. If $\tilde{A}_{\mathrm{int}}$ denotes the matrix in the left-hand member of Eq. (36), the $\mathcal{R}$ operator over the external surface of the cluster is given at specified energy ε by

$$\mathcal{R} = f_{\mathrm{ext}} (\tilde{A}_{\mathrm{int}})^{-1} f_{\mathrm{ext}}^\dagger \ , \tag{38}$$

such that

$$\eta_{\text{ext}}=\mathcal{R}\xi_{\text{ext}} \ . \tag{39}$$

Equation (39) determines the scattering matrix in the external region for electron scattering by a cluster of atomic cells.

Similar equations can be derived for $\mathcal{R}^{-1}$, using Dirichlet boundary conditions in the derivation. The modified variational equations are

$$\widetilde{B}_{\text{int}}c=(g^{\dagger}\eta)_{\text{ext}} \ , \tag{40}$$

where

$$\begin{aligned}\widetilde{B}_{\mathrm{I,I}}&=B_{\mathrm{I,I}}-\tfrac{1}{2}(f^{\dagger}g+g^{\dagger}f)^{\text{int}}_{\mathrm{I,I}} \ ,\\ \widetilde{B}_{\mathrm{I,II}}&=-\tfrac{1}{2}(f^{\dagger}g+g^{\dagger}f)_{\mathrm{I,II}} \ ,\\ &\vdots\end{aligned} \tag{41}$$

The operator $\mathcal{R}^{-1}$ is given by

$$\mathcal{R}^{-1}=g_{\text{ext}}(\widetilde{B}_{\text{int}})^{-1}g^{\dagger}_{\text{ext}} \tag{42}$$

such that

$$\xi_{\text{ext}}=\mathcal{R}^{-1}\eta_{\text{ext}} \ . \tag{43}$$

IV. USE OF STRUCTURE CONSTANTS

Discontinuities across cell interfaces are associated with the nondiagonal blocks of Eqs. (32) or (33). The sum of the off-diagonal terms (I,II) in Eq. (33) is

$$\begin{aligned}&\tfrac{1}{2}c^{\dagger}_{\mathrm{I}}(f^{\dagger}g+g^{\dagger}f)c_{\mathrm{II}}+\tfrac{1}{2}c^{\dagger}_{\mathrm{II}}(f^{\dagger}g+g^{\dagger}f)c_{\mathrm{I}}\\ &\qquad=\tfrac{1}{2}(F^{\dagger}_{\mathrm{I}}G_{\mathrm{II}}+G^{\dagger}_{\mathrm{I}}F_{\mathrm{II}}+F^{\dagger}_{\mathrm{II}}G_{\mathrm{I}}+G^{\dagger}_{\mathrm{II}}F_{\mathrm{I}}) \ ,\end{aligned} \tag{44}$$

where

$$\begin{aligned}&F_{\mathrm{I}}=f_{\mathrm{I}}c_{\mathrm{I}},\ F_{\mathrm{II}}=f_{\mathrm{II}}c_{\mathrm{II}} \ ,\\ &G_{\mathrm{I}}=g_{\mathrm{I}}c_{\mathrm{I}},\ G_{\mathrm{II}}=g_{\mathrm{II}}c_{\mathrm{II}} \ .\end{aligned} \tag{45}$$

If both basis sets $\{\phi_i\}$ and $\{\phi_{\mathrm{II}}\}$ are complete for representation of surface functions, and if the variational functions and derivatives are continuous,

$$\begin{aligned}&F_{\mathrm{I}}=F_{\mathrm{II}}=F \ ,\\ &G_{\mathrm{I}}=-G_{\mathrm{II}}=G \ .\end{aligned} \tag{46}$$

In this case, the sum in Eq. (44) is

$$\tfrac{1}{2}F^{\dagger}(G_{\mathrm{II}}+G_{\mathrm{I}})+\tfrac{1}{2}(G^{\dagger}_{\mathrm{I}}+G^{\dagger}_{\mathrm{II}})F=0 \ . \tag{47}$$

In cellular methods, discontinuous basis functions are used, but a large basis set is required to make the interface terms small.

An alternative method, used in multiple scattering theory[5-7] is to match the cellular basis functions onto well-defined continuous functions whose extension throughout the lattice or cluster is known. This defines contracted basis functions throughout the cluster as specific linear combinations of cellular basis functions within each cell.

The LMTO and LACO methods use auxiliary functions whose values and normal gradients on the boundary of cell Ω are given by

$$\Phi_L(\mathbf{k})=N_L-\Sigma_{L'}J_{L'}\widetilde{S}_{L'L}(\mathbf{k}) \tag{48}$$

for a monatomic periodic solid. Here, index L groups together l, m, and cell site. The functions J_L and N_L, respectively, are regular and irregular solid harmonics. The Hermitian matrix of structure constants $\widetilde{S}_{L'L}(\mathbf{k})$ is determined so that $\Phi_L(\mathbf{k})$, on the surface of the lattice cell of origin, is the representation of a Bloch wave constructed from N_L and its translational images. For a polyatomic translational cell, $\Phi_L(\mathbf{k})$ includes contributions of N_L at one specified site to the J_L sum in other atomic cells within the translational cell.

The orbital basis consists of functions ϕ computed at a base energy E_0 and their energy derivatives $\dot{\phi}$. The surface function values, denoted, respectively, by f and $\dot{f}$ are combined in the contracted functions $\phi+\dot{\phi}\omega$ so that

$$f(\mathbf{k})=f+\dot{f}\omega(\mathbf{k}) \ . \tag{49}$$

The coefficient matrix $\omega(\mathbf{k})$ is obtained by solving a set of energy-independent linear equations

$$F^{\dagger}(\mathbf{k})g(\mathbf{k})-G^{\dagger}(\mathbf{k})f(\mathbf{k})=0 \ , \tag{50}$$

suppressing indices L and L'. The values of $\Phi_L(\mathbf{k})$ and of its weighted outward normal gradient on the local cell boundary are denoted here by $F(\mathbf{k})$ and $G(\mathbf{k})$, respectively.

Expanded about E_0, the energy-dependent matrix A takes the form $A_0-\varepsilon S_0$, where $\varepsilon=E-E_0$ and S_0 is an energy-independent overlap matrix. The matrices A_0 and $f^{\dagger}g$ of Eq. (24) and the matrix S_0 are computed in the basis of functions $\phi,\dot{\phi}$. In the contracted basis for specified $\mathbf{k}$, Eq. (24) is a non-Hermitian linear eigenvalue equation for the energy levels $\varepsilon(\mathbf{k})$. It was found in trial calculations[3,4] that the matrix $A-f^{\dagger}g$ in Eq. (24) could be replaced by its Hermitian part, which is the matrix in the left-hand member of Eq. (28). This substitution had no significant effect on computed energy levels. This result is now explained because the inhomogeneous part of Eq. (28) is reduced to zero except for higher spherical harmonic terms by Eq. (50) in the contracted basis.

For a polyatomic translational cell, the multiple scattering theory uses structure constants exactly as for a monatomic cell. It has been shown that use of structure constants from the Bloch-wave construction removes the lower-order terms of the spherical harmonic expansion of the surface term in Eq. (28). Similarly, the $J_{L'}$ sum of Eq. (48) in each atomic cell represents a smooth continuation of the function Φ_L outside its cell of definition. Hence, the contracted off-diagonal blocks of Eq. (32) must also vanish in the limit of spherical harmonic completeness when structure constants are used for a polyatomic translational cell. The appropriate energy-band equations are then the contracted form of Eq. (32) for the atomic cluster representing a translational cell, omitting off-diagonal blocks and external boundary terms. These equations are currently being used in energy-band calculations of Si.

In considering an atomic cluster, two alternative situations occur. In the first the cluster is isolated, as in a molecular bound state or electron-scattering problem. In these circumstances, the indicated procedure is to use nontranslational structure constants within the cluster. These structure constants are obtained from the expansion of N_L at any one center in a set of J_L functions about each of the other centers. The matrix in Eq. (36) should be computed in the $\phi,\dot{\phi}$ basis, then contracted, omitting off-diagonal blocks such as $\underline{\tilde{A}}_{\mathrm{I,II}}$. The $\mathcal{R}$ operator on the external surface of the cluster is given by Eq. (38) in terms of the contracted matrix $\underline{\tilde{A}}_{\mathrm{int}}$. Bound and continuum states are obtained by matching to external wave functions of the correct asymptotic form using Eq. (39).

If an atomic cluster is embedded in a substrate, the boundary conditions at the matching surface must be determined self-consistently. Continuity conditions at internal interfaces of the cluster can be treated by use of nontranslational structure constants, as for an isolated cluster. The indicated method is to use Eq. (32) in a contracted basis, omitting off-diagonal blocks but not the boundary terms. These boundary terms act as a coupling Hamiltonian when ξ and η are expanded in basis functions of the substrate. By use of structure constants, the variational equations are linearized in energy over a range of energies, so that density-matrix methods[13] may be used, valid within this energy range.

V. DISCUSSION

Variational principles applicable to clusters of space-filling atomic cells have been derived here and related to previous derivations. It is shown that the variational theory of the $\mathcal{R}$ operator for a closed cell corresponds to solution of the classical Neumann boundary problem for the Schrödinger equation in that cell. Similarly, the theory of the inverse operator $\mathcal{R}^{-1}$ corresponds to the analogous classical Dirichlet boundary problem. The variational equations of these two alternative derivations are combined here to give a system of equations for clusters of atomic cells. These equations are consistent with earlier variational equations for discontinuous wave functions.

The use of structure constants, as in multiple scattering theory, can be considered as a device to eliminate the surface integrals required for discontinuous basis functions. By introducing energy-independent structural constants, the variational equations are linearized in energy over a range of energies. For bound states, this replaces root-search methods by the more efficient linear eigenvalue problem of an Hermitian matrix. $\mathcal{R}$-operator scattering calculations that require matrix diagonalization are facilitated.

The principal new formal result here is a variational prescription, incorporating structure constants, for each of two distinct classes of applications. The first class is electron scattering by an isolated cluster, or computation of bound states using scattering theory. The second class is the problem of embedding a cluster in a substrate.

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