

## R-matrix formalism for local cells of arbitrary geometry

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The  $R$  matrix of Wigner and Eisenbud has been widely used in nuclear scattering theory and in the theory of electron scattering by atoms and molecules. To consider problems in solid-state or surface physics, where atoms are in complex environments, this theory must be put into a form that is valid for volumes enclosed by surfaces of arbitrary shape. A variational principle for an  $\mathcal{R}$  operator in general geometry is derived. This operator relates function values to normal derivatives on a surface  $\Sigma$  of a closed volume  $\Omega$  inside which the function satisfies Schrödinger's equation. Using a spherically averaged potential function, the  $\mathcal{R}$  operator for a Wigner-Seitz atomic cell can be computed from solutions of the local radial Schrödinger equation. Formulas that eliminate a common interface between adjacent cells are derived. With these methods, calculations carried out in modular subcells can be extended to larger structures. For regular solids, it is shown that periodic boundary conditions applied to functions and normal derivatives at the surface of a translational unit cell lead to a secular determinant expressed in terms of the  $\mathcal{R}$  operator for the unit cell, whose zeros determine energy-band structure.

### I. INTRODUCTION

The derivative matrix or  $R$  matrix of Wigner and Eisenbud<sup>1,2</sup> is defined as the matrix that transforms first derivatives into function values at a boundary point, for solutions of coupled ordinary second-order differential equations. For functions of a radial variable  $r$ , the defining equation at  $r_0$  is

$$f_{ps}(r_0) = \sum_q R_{pq} r_0 f'_{qs}(r_0). \quad (1)$$

Here  $f_{ps}(r)$  is the solution  $s$  in channel  $p$  of the coupled equations, and  $R_{pq}$  is the  $R$  matrix. Developed for electron scattering calculations by Burke and collaborators,<sup>3</sup>  $R$ -matrix theory has been used for many calculations of electron scattering by atoms and molecules. The existing theory has been used to couple a local variational calculation, inside a spherical boundary, to solutions of the differential equations appropriate to an external vacuum. The generalizations considered here convert this to a theory suitable for cellular models of condensed matter or of impurity or surface environments.

The concept underlying the theory is that Schrödinger's equation is to be solved in a strictly delimited closed volume  $\Omega$ , to obtain information sufficient to match at the enclosing surface  $\Sigma$  to external wave functions. In this way, solution of the Schrödinger equation in the interior of  $\Omega$  is decoupled from the external environment. Different computational techniques or different physical models can be used in the two regions. Adjacent cells can be joined, by eliminating a common interface, to build up complex clusters from modular calculations carried out independently for physically distinct cells.

The required information on surface  $\Sigma$  is embodied in an  $\mathcal{R}$  operator, the linear operator that produces function values on  $\Sigma$  when acting on normal derivatives at this surface, for functions that are solutions of the Schrödinger

equation throughout the enclosed volume  $\Omega$ .

A stationary variational principle for the  $\mathcal{R}$  operator is derived here. Using this variational principle, the  $\mathcal{R}$  operator is constructed by combining matrix elements of a modified Hamiltonian operator, in a basis of linearly independent functions defined in the volume  $\Omega$ , with the values of these basis functions on the enclosing surface  $\Sigma$ . Calculating the  $\mathcal{R}$  operator should be no more difficult than variational solution of the Schrödinger equation with specified boundary conditions.

To show how this theory might be used in practice, a cellular model based on Wigner-Seitz polyhedra is considered here. In muffin-tin and atomic sphere approximations, it is assumed that a spherically averaged potential  $V(r)$  is valid in the neighborhood of each atom in a solid. If it is assumed that this  $V(r)$  is valid throughout the local Wigner-Seitz cell  $\Omega$ , the  $\mathcal{R}$  operator on the cell surface  $\Sigma$  can be evaluated by computing a surface integral over  $\Sigma$ . This development is extended to a polyatomic translational unit cell by deriving equations for concatenating  $\mathcal{R}$  operators for adjacent subcells. Hence the  $\mathcal{R}$  operator for a translational unit cell can be constructed from those computed for constituent atomic cells. Periodicity conditions for a regular lattice can be expressed in terms of the  $\mathcal{R}$  operator for a translational unit cell. A secular determinant is defined whose value must vanish. This condition determines energy-band structure.

### II. VARIATIONAL PRINCIPLE FOR THE $\mathcal{R}$ OPERATOR

Consider a volume  $\Omega$  enclosed by a surface  $\Sigma$ . Using the one-electron Schrödinger Hamiltonian  $h$ , defined throughout  $\Omega$ , at energy  $\epsilon$ , define the volume integral

$$\Xi = \int_{\Omega} \psi^* (h - \epsilon) \psi d\tau \quad (2)$$

$$= A - \frac{1}{2} \int_{\Sigma} \psi^* \nabla_n \psi d\Sigma, \quad (3)$$

where  $\psi$  is a trial wave function and  $\nabla_n\psi$  is its outward normal derivative at  $\Sigma$ . From Eqs. (2) and (3),

$$A = \int_{\Omega} \left[ \frac{1}{2} \vec{\nabla} \psi^* \cdot \vec{\nabla} \psi + \psi^* (V - \epsilon) \psi \right] d\tau, \quad (4)$$

such that the matrix

$$A_{ab} = \int_{\Omega} \left[ \frac{1}{2} \vec{\nabla} \phi_a^* \cdot \vec{\nabla} \phi_b + \phi_a^* (V - \epsilon) \phi_b \right] d\tau \quad (5)$$

is Hermitian in any representation basis, if the potential function  $V$  is real.

If  $\psi$  and  $\nabla_n\psi$  are given on the enclosing surface  $\Sigma$ , the  $\mathcal{R}$  operator is defined by

$$\psi(1) = \int_{\Sigma} \mathcal{R}(1,2) \nabla_n \psi(2) d\Sigma_2, \quad (6)$$

which will be symbolized here by

$$\psi = \mathcal{R} \nabla_n \psi. \quad (7)$$

Considering the function  $\xi$  as given on  $\Sigma$ , boundary conditions that determine a solution of the Schrödinger equation throughout  $\Omega$  are

$$\nabla_n \psi = \xi, \quad \text{on } \Sigma, \quad (8)$$

or, given  $\mathcal{R}$ ,

$$\psi = \mathcal{R} \xi \quad \text{on } \Sigma. \quad (9)$$

When  $\xi$  is specified, the boundary integral

$$A_1 = \frac{1}{2} \int_{\Sigma} \psi^* \xi d\Sigma \quad (10)$$

is defined.

For an exact solution of the Schrödinger equation in  $\Omega$ , the functional  $\Xi$  of Eq. (2) must vanish, which implies that  $A_1$  and  $A$  are equal, and because  $A$  is real,

$$A = A_1 = A_1^*. \quad (11)$$

Infinitesimal variations of  $\psi$  about an exact solution give

$$\delta A = \text{Re} \left[ 2 \int_{\Omega} \delta \psi^* (h - \epsilon) \psi d\tau + \int_{\Sigma} \delta \psi^* \nabla_n \psi d\Sigma \right], \quad (12)$$

and

$$\delta A_1 = \frac{1}{2} \int_{\Sigma} \delta \psi^* \xi d\Sigma. \quad (13)$$

In analogy to the Schwinger variational principle of scattering theory, consider the functional

$$[A] = A_1 A^{-1} A_1^*, \quad (14)$$

which is real for any trial function. From Eqs. (12) and (13)

$$\delta[A] = [A] \text{Re} \left[ A_1^{-1} \int_{\Sigma} \delta \psi^* \xi d\Sigma - A^{-1} \left[ \int_{\Sigma} \delta \psi^* \nabla_n \psi d\Sigma + 2 \int_{\Omega} \delta \psi^* (h - \epsilon) \psi d\tau \right] \right]. \quad (15)$$

From Eq. (11), for variations about an exact solution, Eq. (15) reduces to

$$\delta[A] = \text{Re} \left[ \int_{\Sigma} \delta \psi^* (\xi - \nabla_n \psi) d\Sigma - 2 \int_{\Omega} \delta \psi^* (h - \epsilon) \psi d\tau \right]. \quad (16)$$

Since variations of  $\psi$  are unconstrained throughout  $\Omega$  and on  $\Sigma$ , Eq. (16) implies the variational theorem:  $\delta[A] = 0$  if and only if

$$(i) (h - \epsilon)\psi = 0 \quad \text{in } \Omega, \quad (17)$$

$$(ii) \nabla_n \psi = \xi \quad \text{on } \Sigma.$$

Equations (17) implicitly determine an  $\mathcal{R}$  operator. To make this explicit, introduce a basis  $\{\phi_a\}$  of functions that are linearly independent in  $\Omega$ . Then

$$\psi = \sum_a \phi_a c_a, \quad (18)$$

$$\delta \psi = \sum_a \phi_a \delta c_a. \quad (19)$$

When expressed in this basis, if  $\delta[A]$  vanishes, Eq. (16) implies

$$\sum_b \int_{\Omega} \phi_a^* (h - \epsilon) \phi_b d\tau c_b = \frac{1}{2} \int_{\Sigma} \phi_a^* \left[ \xi - \sum_b \nabla_n \phi_b c_b \right] d\Sigma, \quad (20)$$

or, integrating by parts and using Eq. (5),

$$\sum_b A_{ab} c_b = \frac{1}{2} (a | \xi)_{\Sigma}, \quad \text{all } a, \quad (21)$$

where

$$(a | \xi)_{\Sigma} = \int_{\Sigma} \phi_a^* \xi d\Sigma. \quad (22)$$

Hence, explicitly,

$$c_b = \frac{1}{2} \sum_a [A^{-1}]_{ba} (a | \xi)_{\Sigma}, \quad \text{all } b. \quad (23)$$

When these values are substituted into Eqs. (4), (10), and (14), it turns out that

$$[A] = A = A_1 = A_1^* \quad (24)$$

$$= \frac{1}{4} \sum_a \sum_b (\xi | a)_{\Sigma} [A^{-1}]_{ab} (b | \xi)_{\Sigma}. \quad (25)$$

In terms of the  $\mathcal{R}$  operator, Eq. (10) is

$$A_1 = \frac{1}{2} \int \int \xi^*(1) \mathcal{R}(1,2) \xi(2) d\Sigma_2 d\Sigma_1. \quad (26)$$

Comparison with Eq. (25) indicates that

$$\mathcal{R}(1,2) = \frac{1}{2} \sum_a \sum_b \phi_a(1) [A^{-1}]_{ab} \phi_b^*(2), \quad (27)$$

which must hold for all points 1,2 on surface  $\Sigma$ , because the function  $\xi$  is arbitrary.

Equation (27) is the principal result of the present paper. Because  $[A]$  is stationary and the surface function  $\xi$  is arbitrary, the  $\mathcal{R}$  operator itself is stationary. It is evidently real and symmetric. The basis functions  $\{\phi_a\}$  are required only to be linearly independent in  $\Omega$ . In fact, re-

quiring orthonormality through a fixed boundary condition on  $\Sigma$  imposes a *lack* of completeness with respect to determining the  $\mathcal{R}$  operator.<sup>4</sup> Equation (27) is familiar in electron-atom scattering theory,<sup>3,4</sup> but in a slightly different form, since radial basis functions are multiplied by  $r$  for use in spherical polar coordinates. This  $r$  multiplication modifies the apparent boundary term in Eqs. (3) and (16) and introduces the factor  $r_0$  in the standard definition of the  $R$  matrix, Eq. (1). The present derivation is independent of choice of coordinate system.

### III. CONCATENATION OF ADJACENT CELLS

As applied to ordinary differential equations with a progressive independent variable  $r$ , an  $R$  matrix at  $r_0$  can be propagated to successive coordinate values  $r_1, r_2, \dots$ . As shown by Light and Walker,<sup>5</sup> this can be done by considering two-sided  $R$  matrices appropriate to the successive coordinate intervals. Adjacent intervals are concatenated by eliminating reference to functions of the shared intermediate coordinate value. This procedure is generalized here for adjacent cells of arbitrary geometrical shape.

Consider adjacent cells  $\Omega_1$  (surface  $\Sigma_1$  plus  $\Sigma_{2+}$ ) and  $\Omega_3$  (surface  $\Sigma_3$  plus  $\Sigma_{2-}$ ), where  $\Sigma_{2+}$  and  $\Sigma_{2-}$  refer to the common interface of  $\Omega_1$  and  $\Omega_3$ , but with outward normal directed oppositely in the two cases. The defining equations for the  $\mathcal{R}$  operator are

$$\begin{aligned}\psi_1 &= \int \mathcal{R}_{11} \nabla_n \psi_1 d\Sigma_1 + \int \mathcal{R}_{12+} \nabla_n \psi_2 d\Sigma_{2+}, \\ \psi_2 &= \int \mathcal{R}_{2+1} \nabla_n \psi_1 d\Sigma_1 + \int \mathcal{R}_{2+2+} \nabla_n \psi_2 d\Sigma_{2+}, \\ \psi_2 &= \int \mathcal{R}_{2-3} \nabla_n \psi_3 d\Sigma_3 + \int \mathcal{R}_{2-2-} \nabla_n \psi_2 d\Sigma_{2-}, \\ \psi_3 &= \int \mathcal{R}_{33} \nabla_n \psi_3 d\Sigma_3 + \int \mathcal{R}_{32-} \nabla_n \psi_2 d\Sigma_{2-}.\end{aligned}\quad (28)$$

The two equations for  $\psi_2$  can be combined to give an integral equation for  $\nabla_n \psi_2$ . Using

$$\nabla_n \psi_{2-} = -\nabla_n \psi_{2+}, \quad (29)$$

it follows that

$$\begin{aligned}\int (\mathcal{R}_{2+2+} + \mathcal{R}_{2-2-}) \nabla_n \psi_2 d\Sigma_2 \\ = - \int \mathcal{R}_{2+1} \nabla_n \psi_1 d\Sigma_1 + \int \mathcal{R}_{2-3} \nabla_n \psi_3 d\Sigma_3.\end{aligned}\quad (30)$$

Assuming that the linear operator  $\mathcal{R}_{2+2+} + \mathcal{R}_{2-2-}$  is non-singular, its inverse is defined and Eqs. (28) reduce to the form

$$\begin{aligned}\psi_1 &= \int \tilde{\mathcal{R}}_{11} \nabla_n \psi_1 d\Sigma_1 + \int \tilde{\mathcal{R}}_{13} \nabla_n \psi_3 d\Sigma_3, \\ \psi_3 &= \int \tilde{\mathcal{R}}_{31} \nabla_n \psi_1 d\Sigma_1 + \int \tilde{\mathcal{R}}_{33} \nabla_n \psi_3 d\Sigma_3,\end{aligned}\quad (31)$$

where

$$\begin{aligned}\tilde{\mathcal{R}}_{11} &= \mathcal{R}_{11} - \mathcal{R}_{12+} (\mathcal{R}_{2+2+} + \mathcal{R}_{2-2-})^{-1} \mathcal{R}_{2+1}, \\ \tilde{\mathcal{R}}_{13} &= \mathcal{R}_{12+} (\mathcal{R}_{2+2+} + \mathcal{R}_{2-2-})^{-1} \mathcal{R}_{2-3}, \\ \tilde{\mathcal{R}}_{31} &= \mathcal{R}_{32-} (\mathcal{R}_{2+2+} + \mathcal{R}_{2-2-})^{-1} \mathcal{R}_{2+1}, \\ \tilde{\mathcal{R}}_{33} &= \mathcal{R}_{33} - \mathcal{R}_{32-} (\mathcal{R}_{2+2+} + \mathcal{R}_{2-2-})^{-1} \mathcal{R}_{2-3}.\end{aligned}\quad (32)$$

If  $\Omega_3$  is contained within  $\Omega_1$ , sharing a common outer boundary  $\Sigma_2$  with outward normal vectors pointing in the same direction, similar equations can be derived. Equations differ in the two cases only by sign changes due to the different definitions of outward normal. This process could be used, for example, to eliminate the common sector of two overlapping atomic spheres.

The operator inverse required in Eqs. (32) can be represented as a matrix inverse in a local basis of surface functions on  $\Sigma_2$ . Appropriate surface basis functions might be projections of spherical harmonics or finite elements.

### IV. ATOMIC-SPHERE MODEL FOR A WIGNER-SEITZ CELL

Consider a potential function  $V(r)$ , spherically averaged about a given atom. This is a working assumption in several standard methods of energy-band theory. In particular, in the atomic-sphere approximation,<sup>6</sup> as in the original cellular method, this averaged potential is assumed to be valid throughout an atomic sphere whose volume equals that of the local Wigner-Seitz cell. It will be shown here that the  $\mathcal{R}$  operator for the Wigner-Seitz cell can be computed directly from the radial wave functions of this model.

Consider a Wigner-Seitz cell  $\Omega$  and the local atomic sphere  $S$  of equal volume. Given the spherically averaged potential  $V(r)$ , postulated to be valid throughout  $\Omega$ , the Schrödinger eigenfunctions are of the form

$$f_{lm}(\vec{r}) = \phi_l(r) Y_{lm}(\theta, \phi), \quad (33)$$

where  $\phi_l(r)$  is a radial wave function at a given energy. Normalization in the present theory is arbitrary, since boundary conditions are not imposed except by requiring regularity at  $r=0$ .

The surface  $\Sigma$  of  $\Omega$  can be subdivided into facets  $\Sigma_\alpha, \Sigma_\beta, \dots$ . Functions on a particular facet  $\Sigma_\alpha$  can be represented in terms of displacements from the equivalent sphere  $S$  of radius  $s$ . Since the Wigner-Seitz cell is convex, each point on  $\Sigma_\alpha$  is uniquely defined by polar coordinates  $(\theta, \phi)$  about the atomic center. Radial displacement of a point on  $\Sigma_\alpha$  is defined by

$$r_\alpha(\theta, \phi) = s + \Delta s_\alpha(\theta, \phi), \quad (34)$$

and the displacement of the outward normal vector is defined by

$$\hat{n}_\alpha = \hat{r}(\theta, \phi) + \Delta \hat{n}_\alpha(\theta, \phi). \quad (35)$$

Here  $\hat{n}_\alpha$  is constant for a given plane facet  $\Sigma_\alpha$ . At any point on  $\Sigma_\alpha$ , the value of  $f_{lm}$  is given directly by Eq. (33), and the normal gradient  $\nabla_n f_{lm}$  is easily computed in terms of the radial and transverse components of  $\hat{n}_\alpha$ .

Since the functions  $f_{lm}(\vec{r})$  are local solutions of the Schrödinger equation, matrix elements defined by Eq. (5) reduce to a surface term. In general, as in Eqs. (2) and (3),

$$\int_\Omega \phi_a^*(h - \epsilon) \phi_b d\tau = A_{ab} - \frac{1}{2} \int_\Sigma \phi_a^* \nabla_n \phi_b d\Sigma. \quad (36)$$

Hence, for the functions  $f_{lm}(\vec{r})$ ,

$$A_{lm,l'm'} = \frac{1}{2} \int_{\Sigma} f_{lm}^* \nabla_n f_{l'm'} d\Sigma. \quad (37)$$

Using Eqs. (34) and (35), the required integral can be represented for each facet as an integral in polar coordinates  $(\theta, \phi)$ . Given values of the matrix elements, Eq. (37), and values of  $f_{lm}$  evaluated on  $\Sigma_\alpha$ , the  $\mathcal{R}$  operator is given by Eq. (27) in the form

$$\mathcal{R}(1,2) = \frac{1}{2} \sum_{l,m} \sum_{l',m'} f_{lm}(1) [A^{-1}]_{lm,l'm'} f_{l'm'}^*(2). \quad (38)$$

for points (1,2) on  $\Sigma$ .

## V. PERIODIC BOUNDARY CONDITIONS

Consider a polyhedral translational unit cell  $\Omega$ , enclosed by surface  $\Sigma$  and assume that the  $\mathcal{R}$  operator is known. Translational invariance requires that  $\Sigma$  should consist of sets of paired facets that displace into each other. A particular pair of facets  $\Sigma_\alpha, \Sigma_\beta$  can be labeled such that points on  $\Sigma_\beta$  are obtained from matched points on  $\Sigma_\alpha$  by translation vector  $\vec{\tau}_{\alpha\beta}$ . At a given one-electron energy  $\epsilon$  and wave vector  $\vec{k}(\epsilon)$ , the translation conditions on periodic wave functions are

$$f(\beta) = e^{i\vec{k} \cdot \vec{\tau}} f(\alpha), \quad (39)$$

$$\nabla_n f(\beta) = -e^{i\vec{k} \cdot \vec{\tau}} \nabla_n f(\alpha), \quad (40)$$

for matched points  $\alpha, \beta$  and translation vector  $\vec{\tau}_{\alpha\beta}$ .

If the enclosing surface is divided into two half-surfaces  $A$  (all facets  $\Sigma_\alpha$ ) and  $B$  (all facets  $\Sigma_\beta$ ), then the combination of  $\mathcal{R}$ -operator definition and translation conditions gives two distinct expressions for  $f(A)$ , evaluated at some point of half-surface  $\Sigma_A$ ,

$$f(A) = \int [\mathcal{R}_{AA'} - \mathcal{R}_{AB} e^{i\vec{k} \cdot \vec{\tau}'}] \nabla_n f(A') d\Sigma'_A, \quad (41)$$

and

$$\begin{aligned} f(A) &= e^{-i\vec{k} \cdot \vec{\tau}} f(B) \\ &= \int e^{-i\vec{k} \cdot \vec{\tau}} [\mathcal{R}_{BA'} - \mathcal{R}_{BB} e^{i\vec{k} \cdot \vec{\tau}'}] \nabla_n f(A') d\Sigma'_A. \end{aligned} \quad (42)$$

Here  $B$  denotes a point on half-surface  $\Sigma_B$ , matched to point  $A$ , and similarly for  $B'$  and  $A'$ . Consistency between Eqs. (41) and (42) requires

$$\begin{aligned} \int [\mathcal{R}_{AA'} - \mathcal{R}_{AB} e^{i\vec{k} \cdot \vec{\tau}'} - e^{-i\vec{k} \cdot \vec{\tau}} \mathcal{R}_{BA'} \\ + e^{-i\vec{k} \cdot \vec{\tau}} \mathcal{R}_{BB} e^{i\vec{k} \cdot \vec{\tau}'}] \nabla_n f(A') d\Sigma'_A = 0, \end{aligned} \quad (43)$$

for all points on  $\Sigma_A$ .

This integral equation can be converted to algebraic equations by expanding functions and operators in a basis of surface functions or finite elements. The vector  $\vec{k}(\epsilon)$  is to be chosen so that the determinant of these algebraic equations is zero. This determines  $\nabla_n f$  on half-surface  $\Sigma_A$ , except for normalization. Then  $\nabla_n f$  is determined on  $\Sigma_B$  by translation, and the surface values of  $f$  are determined by the  $\mathcal{R}$ -operator equations. Thus a full solution of the periodic potential problem is obtained, except for normalization, if  $\vec{k}(\epsilon)$  is chosen so that the secular deter-

minant of Eq. (43) vanishes.

It should be noted that, because the equations refer only to a half-surface, the number of algebraic equations derived from Eq. (43) in a basis representation is equal to the number of unknown coefficients. Hence the algebraic equations are nonsingular except for specific choices of  $\vec{k}(\epsilon)$ .

## VI. DISCUSSION

This paper has presented a development of the  $R$ -matrix theory that is intended to open up new applications of this theory to studies of electrons in complex environments, relevant to solid-state and surface physics. A variational principle has been derived for an  $\mathcal{R}$  operator appropriate to any closed volume  $\Omega$  with enclosing surface  $\Sigma$ . The variational principle gives a stationary expression for the  $\mathcal{R}$  operator, expressed in terms of basis functions required only to be linearly independent in  $\Omega$ .

Equations required to concatenate adjacent volume cells have been derived, making it possible to build up the  $\mathcal{R}$  operator for a complex cluster from  $\mathcal{R}$  operators for simpler subcells. To illustrate use of this methodology, the  $\mathcal{R}$  operator for a Wigner-Seitz atomic cell is derived, assuming that a spherically averaged potential function is valid within the cell. Periodic boundary conditions, in conjunction with the defining equations of the  $\mathcal{R}$  operator for a translational unit cell, lead to a secular determinant condition that determines energy-band structure of a periodic solid.

The development given here, valid for Wigner-Seitz polyhedra, in principle solves the problem of overlapping spheres inherent in the atomic-sphere approximation. The further step of incorporating nonspherical terms in the local potential is straightforward. If nonspherical effects are relatively small, the eigenfunctions  $f_{lm}$  of a spherical potential can be used as variational basis functions. From Eqs. (5) and (27), only incremental matrix elements  $(lm | \Delta V | l'm')_\Omega$  have to be computed, where  $\Delta V$  is the nonspherical potential and  $\Omega$  is a Wigner-Seitz cell. Integrals  $(lm | \Delta V | l'm')_S$  over the equivalent local sphere reduce to sums of radial integrals multiplied by vector-coupling coefficients. The difference between the required integral over  $\Omega$  and the corresponding integral over  $S$  can be computed as if it were a surface integral, by use of Eqs. (34) and (35), if  $\Delta s_\alpha$  and  $\Delta \hat{n}_\alpha$  are fitted over each facet of the Wigner-Seitz cell by low-order polynomials.

It is interesting to compare the present  $\mathcal{R}$ -operator formalism with the Green-function method of Inglesfield.<sup>7,8</sup> Green functions for complex clusters can be built up from those for simpler elementary cells (or for a periodic substrate) by eliminating common interfaces between adjacent cells.<sup>7</sup> This method has been applied to problems in surface physics.<sup>8</sup>

The Green function  $G_\Omega(\vec{r}, \vec{r}')$  for a closed volume  $\Omega$  is only defined when boundary conditions are specified on the enclosing surface  $\Sigma$ . In contrast, the  $\mathcal{R}$  operator provides a consistency condition for boundary values of  $\psi$  and  $\nabla_n \psi$ , but does not itself depend on a specific choice of these boundary values. The  $\mathcal{R}$  operator computed for a local cell  $\Omega$  suffices for boundary matching to any exter-

nal wave function. Hence the  $\mathcal{R}$  operator is modular in a much stricter sense than is the corresponding Green function. In detail, the embedding potential that modifies a local Schrödinger equation in the method of Inglesfield<sup>7</sup> depends on the external environment, while the variational equations for the  $\mathcal{R}$  operator make no reference to this environment.

Another apparent advantage of the present approach is that the  $\mathcal{R}$  operator relates two points on the surface  $\Sigma$ , while the Green function relates two points in the enclosed volume  $\Omega$ . This reduces six coordinates to four in general geometry, which should simplify calculations in which these operators must be represented explicitly.

The most efficient computational implementation of the present formalism remains to be developed. The basic variational equations are no more complicated in principle

than those that determine a variational solution of Schrödinger's equation with fixed boundary conditions. While energy-dependent basis functions, regular solutions of a radial Schrödinger equation, have been used here to derive the  $\mathcal{R}$  operator for a Wigner-Seitz atomic cell, an energy-independent basis could have been used. This would require evaluation of energy-independent volume integrals rather than energy-dependent surface integrals, but might be the more efficient procedure in practice. Various computational options will be considered in exploratory calculations with the proposed methodology.

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