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Green's-function methods for electronic-structure calculations

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Two contributions to the Green's-function formulation of electronic-structure calculations are described. We show that a seemingly minor change in the definition of the relevant perturbed and unperturbed Green's functions eliminates several problems that have hampered development of the formalism. Defining the Green's functions in terms of matrices, rather than differential operators, substantially simplifies the description of many systems, including displaced atoms, transition-metal impurities in non-transition-metal hosts, and chemisorbed atoms. In particular, our methods provide a natural solution to the so-called cluster-embedding problem. The second development we describe pertains to the summation over the occupied states of a system that is required in order to construct quantities such as the total energy and the electron density. We show that these summations, which are an essential part of self-consistent calculations, can be represented as contour integrals and that certain displacements of the contour lead to a significant simplification of the calculations.

I. INTRODUCTION

Electronic-structure calculations allow us to understand the macroscopic properties of polyatomic systems in terms of the microscopic states available to the electrons. The approximate treatment of exchange and correlation provided by the local-density approximation[1,2] has now been tested on a variety of systems, and the success of these calculations for relatively small systems[3,4] (and systems such as elemental solids[5,6] that are effectively small because of their high symmetry) justifies the expectation that electronic-structure analysis can be usefully applied to more complex problems, such as atoms[7,8] and small molecules[9] interacting with solid surfaces. For these larger systems it is frequently of greater interest to know the *change* in the electronic structure associated with a change of atomic position[10] or the presence of additional atom(s)[7] than it is to know the electronic structure *per se*. This paper is concerned with the development of a theoretical technique that makes possible the direct calculation of such changes. Examples of the types of physical problems for which this kind of analysis is appropriate are the following: solid surfaces, vacancies, voids, and impurity atoms in solids, the chemisorption of atoms and molecules on solid surfaces, the formation of molecules from atoms, and the effects of atomic displacements in molecules and solids.

This paper describes contributions to the scattering-theoretic or Green's-function method[11–31] of electronic-structure calculations. This method permits the study of a complicated system by representing it as a relatively simple system plus a difference. Perhaps the simplest example of a system to which the Green's-function approach is well suited is that of a substitutional impurity in an otherwise perfect crystalline solid. Such a problem lacks the translational symmetry that underlies the study (energy-band theory) of perfect crystals. The Green's-function approach renders the substitutional-impurity problem tractable by regarding it as a perfect crystal plus a spatially restricted difference.

Many important problems are characterized by the fact that only a small portion of a large system is relevant to the physical phenomena we are trying to understand, the region surrounding a substitutional impurity in a crystal, for example. This fact has led to efforts to study such systems by approximating them as small finite systems. For example, crystal surfaces are frequently studied by approximating the (effectively) semi-infinite crystal as a "slab" of the material several atomic layers thick,[32–34] but infinite in both directions parallel to the surface. Similarly, point defects, such as substitutional impurities, have been studied with the use of clusters of several atoms to simulate the (effectively) infinite system.[35–37] Such procedures do not exploit the relative simplicity of the perfect crystal to which they are related, and they are also hindered by the fact that individual electronic states are affected over a much larger range than are properties, such as the total energy or electron density, that reflect the combined effect of many individual electron states. The Green's-function approach exploits this distinction, whereas the cluster and slab approximations do not. The degree of symmetry loss associated with different types of perturbations is of great practical importance here. A surface destroys translational symmetry in only one dimension, whereas a point defect destroys it in all three. This distinction has resulted in the continued effective use of the slab approximation for surfaces, whereas it has proven necessary to develop Green's-function methods for the application of density-functional theory to vacancies and other point defects. For semiconductors, the work of Pantelides and co-workers[27,38] and that of Baraff, Schlüter, and Kane[28,39,40] have already brought this development to a state of considerable refinement.

A final distinction between the Green's-function and cluster (slab) approaches is that perturbation-induced effects such as surface states, and levels in the gaps of semiconductors, are referenced to bulk properties, such as band edges, in the Green's-function approach. Only with substantial effort are such aspects of the electronic structure of the perfect crystal regained in the cluster (slab) approaches.[35]

II. MATRICES VERSUS DIFFERENTIAL OPERATORS

This section is concerned with the precise meaning of the term Green's function as we will use it in this paper. We begin with a single-particle Hamiltonian H such as that appearing in the Schrödinger equation that must be solved in density-functional theory,[1,2]

$$H\psi_i=\epsilon_i\psi_i \; , \tag{1}$$

or, more explicitly (in atomic units),

$$[-\tfrac{1}{2}\nabla^2+V(\vec{r})-\epsilon_i]\psi_i(\vec{r})=0 \; . \tag{2}$$

We approximate the wave-function solutions of Eq. (2) by an expansion in a *finite* set of basis functions $\{\varphi_\nu(\vec{r})\}$,

$$\psi_i(\vec{r})\cong\sum_{\nu=1}^{\nu=N}c_{i\nu}\varphi_\nu(\vec{r}) \; . \tag{3}$$

We use the symbol $\cong$ in Eq. (3) in order to contrast Eq. (3) with the formally exact relationships we derive below. Note, however, that the imprecision of Eq. (3) is due only to the finiteness of the basis set $\{\varphi_\nu(\vec{r})\}$; the numerical error caused by this finiteness can always be made acceptably small by increasing N. The expansion coefficients $c_{i\nu}$ indicate a transformation, but not a unitary transformation, because the functions $\{\varphi_\nu(\vec{r})\}$ possess no special normalization or orthogonality properties. The defining property of the expansion coefficients $c_{i\nu}$ is their ability to diagonalize both the normalization *matrix* $S_{\nu\nu'}$, and the Hamiltonian *matrix* $H_{\nu\nu'}$. That is,

$$\sum_{\nu\nu'}c_{i\nu}^{*}S_{\nu\nu'}c_{j\nu'}=\delta_{ij} \; , \tag{4}$$

where $S_{\nu\nu'}$ is the normalization matrix for the functions $\{\varphi_\nu(\vec{r})\}$,

$$S_{\nu\nu'}\equiv\int d^3r\,\varphi_\nu^{*}(\vec{r})\varphi_{\nu'}(\vec{r}) \; . \tag{5}$$

Similarly,

$$\sum_{\nu\nu'}c_{i\nu}^{*}H_{\nu\nu'}c_{j\nu'}=\epsilon_i\delta_{ij} \; , \tag{6}$$

where

$$H_{\nu\nu'}\equiv\int d^3r\,\varphi_\nu^{*}(\vec{r})[-\tfrac{1}{2}\nabla^2+V(\vec{r})]\varphi_{\nu'}(\vec{r}) \; . \tag{7}$$

We are now in a position to define the particular Green's function $G_{\nu\nu'}(\epsilon)$ that we find useful:

$$\sum_{\nu''}(\epsilon S_{\nu\nu''}-H_{\nu\nu''})G_{\nu''\nu'}(\epsilon)\equiv\delta_{\nu\nu'} \; , \tag{8}$$

where $S_{\nu\nu'}$ and $H_{\nu\nu'}$ are given by Eqs. (5) and (7). The distinguishing feature of our Green's function is that it is not defined in terms of the *differential operator* $-\frac{1}{2}\nabla^2+V(\vec{r})$; rather; it is simply the inverse of the *matrix* $\epsilon S_{\nu\nu'}-H_{\nu\nu'}$. A fundamental implication of the matrix approach is that the Green's function appropriate to a given physical problem is not uniquely implied by the physical problem alone; it also depends on the choice of expansion set $\{\varphi_\nu(\vec{r})\}$. In the usual (differential-operator) approach a uniquely specified Green's function is approximated more or less accurately depending on the expansion set. In the matrix approach, defining the Green's functions in terms of the matrices that arise in a particular calculation permits all the calculational steps connecting the problem statement (the matrices $H_{\nu\nu'}$ and $S_{\nu\nu'}$) to the final result to be performed without approximation,[41] thereby isolating the basis-set expansion of the wave function [Eq. (3)] as the only approximation made in the solution of the single-particle equations. In Secs. III, IV, and V to follow we show that the exact (matrix) Green's function for an approximate Hamiltonian has several practical advantages over an approximate Green's function for the exact Hamiltonian (differential operator).

Before proceeding to that discussion, however, we demonstrate here that the Green's function defined in Eq. (8) possesses the essential property of permitting the convenient calculation of quantities such as the total energy and the electron density. For the purpose of illustration let us consider as a specific example the quantity T, where

$$T \equiv \sum_i \int d^3r\, \psi_i^*(\vec{r})(-\tfrac{1}{2}\nabla^2)\psi_i(\vec{r}) \times \Theta(\epsilon_F - \epsilon_i) , \qquad (9)$$

where ϵ_F is the Fermi energy and the Heaviside function [$\Theta(x)=1$ for $x>0$, zero otherwise] limits the summation to the occupied states of the system. The expansion of each eigenstate $\psi_i(\vec{r})$ in the common basis set $\{\varphi_\nu(\vec{r})\}$ [Eq. (3)] permits the desired quantity T to be expressed as a trace over a density matrix,

$$T \cong \mathrm{Tr}\{\rho t\} \equiv \sum_{\nu\nu'} \rho_{\nu\nu'} t_{\nu'\nu} , \qquad (10)$$

where

$$t_{\nu\nu'} \equiv \int d^3r\, \varphi_\nu^*(\vec{r})(-\tfrac{1}{2}\nabla^2)\varphi_{\nu'}(\vec{r}) \qquad (11)$$

and the density matrix we want to consider is simply

$$\rho_{\nu\nu'} \equiv \sum_i c_{i\nu}^* c_{i\nu'} \Theta(\epsilon_F - \epsilon_i) . \qquad (12)$$

Note that the expression for T in Eq. (10) does not involve any additional approximations; Eq. (10) is approximate only because the basis set $\{\varphi_\nu(\vec{r})\}$ used in Eq. (3) is finite.

Equation (10) relates the desired quantity T to the density matrix $\rho_{\nu\nu'}$; what remains is to relate $\rho_{\nu\nu'}$ to the Green's function defined by Eq. (8). That the Green's-function matrix can be written as

$$G_{\nu\nu'}(\epsilon) = \sum_i \frac{c_{i\nu} c_{i\nu'}^*}{\epsilon - \epsilon_i} , \qquad (13)$$

can be readily verified by substituting this representation of $G_{\nu\nu'}(\epsilon)$ into Eq. (8), and using the defining properties of the expansion coefficients $c_{i\nu}$ [Eqs. (4) and (6)]. Equation (13) reveals that the required density matrix is obtained from the Green's-function matrix by performing the following contour integration:

$$\rho_{\nu\nu'} = \frac{1}{2\pi i} \int_C dz\, G_{\nu\nu'}(z) , \qquad (14)$$

where the contour C encloses those poles of $G_{\nu\nu'}(z)$ [the ϵ_i in Eq. (13)] corresponding to the occupied states of the system. A more conventional representation of the density matrix results when the contour is collapsed to the real axis.

The density matrix $\rho_{\nu\nu'}$ permits the straightforward evaluation of all the quantities required to construct the total energy and to carry out a self-consistent-field iteration. Note, in particular, that the fact that the basis set is not orthonormal does not complicate the analysis.

III. DYSON EQUATION

Many systems of interest can be regarded as only slightly different from a relatively simple system or as a combination of systems that are individually simple. The great virtue of the Green's-function approach to electronic-structure theory is that it permits us to exploit this relative simplicity, both calculationally and conceptually. The theoretical construct that provides the link between the system of interest and the related simple system(s) is the Dyson equation. In this section we describe the version of the Dyson equation appropriate to the matrix Green's function defined in Sec. II. Perhaps the simplest type of system illustrating the relative simplicity that we want to exploit is a substitutional impurity in an otherwise perfectly crystalline solid. For such a system we regard the corresponding perfect crystal as the related simple system and use the Dyson equation to describe the effects of replacing one of the atoms of the perfect crystal by a different atom. The perfect crystal is enormously easier to study because the translation symmetry causes the analysis to decompose into a set of independent and quite manageable pieces.

Our objective is to construct the Green's-function matrix for the perturbed system (e.g., crystal with impurity). We denote this Green's-function matrix by $G_{\nu\nu'}(\epsilon)$. Denoting the Hamiltonian matrix for the perfect crystal by $H^0_{\nu\nu'}$ and that of the imperfect crystal by $H_{\nu\nu'}$, we define the matrix difference $\delta H_{\nu\nu'}$ as follows:

$$\delta H_{\nu\nu'} \equiv H_{\nu\nu'} - H^0_{\nu\nu'} . \qquad (15)$$

Of course, the straightforward subtraction of the Hamiltonian matrices indicated by Eq. (15) implicitly assumes that $H_{\nu\nu'}$ and $H^0_{\nu\nu'}$ have the same dimension. This one-to-one correspondence of the matrices $H_{\nu\nu'}$ and $H^0_{\nu\nu'}$ is the significance of the substitutional-impurity problem as a generic type. (We consider the other generic types in Secs. IV and

V.) Substitutional impurities (of the same chemical type as the host) do not introduce fundamentally new atomic states into the system; the perturbed and unperturbed systems differ only quantitatively, not qualitatively. Note that the relationship between the number of atomic states and the number of basis functions (the dimension of $H_{\nu\nu'}$) is never a precise one. For a given problem the number of basis functions depends on the degree of precision desired, but, for a given level of precision, there is a general correspondence between the number of atomic states and the size of the basis set required for their description. This correspondence is most explicit when atomic orbitals are used as basis functions.

The subtraction of the perturbed and unperturbed Hamiltonians in Eq. (15) brings out the first substantive implication of the differential-operator—matrix distinction, namely, that the indices $\{\nu\}$ can refer to different sets of functions $\{\varphi_\nu(\vec{r})\}$ in the perturbed and unperturbed problems. For cases in which the unperturbed problem is large or infinite, it will, of course, be of great practical importance that the matrix $\delta H_{\nu\nu'}$ have negligible magnitude for all but a small subset of its indices. Within this subset, however, the functions referred to by a given value of ν can be arbitrarily different in the perturbed and unperturbed problems. For example, if we use free-atom eigenfunctions as our basis functions $\{\varphi_\nu(\vec{r})\}$, then the orbitals associated with the impurity atom will differ from those of the host crystal. As physically well motivated as this basis-set freedom might seem, it is very difficult to use in the conventional differential-operator approach. In empirical tight-binding theory this "chemical" adaptation of the basis set is implicit and automatic; the study of deep traps in covalent semiconductors by Hjalmarson *et al.*[42] illustrates the effectiveness of this adaptation in describing chemical trends. In the context of nonempirical calculations the basis-set freedom available in the matrix approach carries with it the necessity of properly accounting for changes $\delta S_{\nu\nu'}$ in the normalization matrix

$$\delta S_{\nu\nu'} \equiv S_{\nu\nu'} - S^0_{\nu\nu'} \; . \tag{16}$$

The definitions (15) and (16) permit us to proceed directly to the Dyson equation relating the desired Green's-function matrix $G_{\nu\nu'}(\epsilon)$ to the corresponding and presumed known matrix $G^0_{\nu\nu'}(\epsilon)$ for the perfect crystal. We use Eqs. (15) and (16) to substitute for $\epsilon S_{\nu\nu'} - H_{\nu\nu'}$ in Eq. (8), obtaining

$$\sum_{\nu''} [\,(\epsilon S^0_{\nu\nu''} - H^0_{\nu\nu''}) + (\epsilon \delta S_{\nu\nu''} - \delta H_{\nu\nu''})]G_{\nu''\nu'}(\epsilon) = \delta_{\nu\nu'} \; . \tag{17}$$

If we now multiply Eq. (17) by the perfect-crystal Green's-function matrix $G^0_{\nu\nu'}(\epsilon)$ and use its defining property

$$\sum_{\nu''} (\epsilon S^0_{\nu\nu''} - H^0_{\nu\nu''}) G^0_{\nu''\nu'}(\epsilon) \equiv \delta_{\nu\nu'} \; , \tag{18}$$

we obtain our Dyson equation

$$G(\epsilon) = G^0(\epsilon) + G^0(\epsilon)(\delta H - \epsilon \delta S) G(\epsilon) \; , \tag{19}$$

where we have suppressed the $\{\nu\}$ indices. The Dyson equation provides a straightforward means of evaluating the Green's-function matrix $G_{\nu\nu'}(\epsilon)$ and the density matrix $\rho_{\nu\nu'}$. Note, however, that because the orbitals $\{\varphi_\nu(\vec{r})\}$ of the perturbed system are, in general, different from their counterparts for the unperturbed system, the expectation value of an operator such as T considered above must be written

$$T = \mathrm{Tr}[\rho^0 t^0 + (\delta\rho) t^0 + (\delta\rho)\delta t + \rho^0 \delta t] \; , \tag{20}$$

where $\delta t \equiv \delta t_{\nu\nu'}$ is defined in complete analogy with δH and δS [Eqs. (15) and (16)], that is,

$$\delta t_{\nu\nu'} \equiv t_{\nu\nu'} - t^0_{\nu\nu'} \; . \tag{21}$$

As with Eq. (16), the matrix difference $\delta t_{\nu\nu'}$ reflects a change in the orbitals, not in the fundamental operator.

We note that it is the fact that our formalism is based on matrices rather than on differential operators that permitted us to use different orbitals for the perturbed systems without complicating the analysis significantly. In particular, we note that the freedom to use basis functions adapted independently to the perturbed and unperturbed systems does not increase the dimension of any of the matrices required by the theory.

A closely related and probably more important advantage of the matrix approach concerns the description of systems in which one or more of the atoms is displaced. In the matrix approach the basis functions are free to move with the atoms, so that the effect of the atomic displacements is simply to produce small changes in the numerical value of some of the matrix elements. The description of the same physical effect in the usual differential-operator formalism has two disadvantages relative to the matrix approach. First, the subtraction of the perturbed and unperturbed single-particle Hamiltonians to form the perturbation potential yields a very sharply varying function, due to the strength of the single-particle potentials (even many pseudopotentials[40,43]) in the vicinity of each atom. Second, since, in the differential-operator approach, matrices are formed (by introducing a basis set) *after* the Hamiltonians are subtracted, it is not clear whether the basis functions should be centered on the displaced or the undisplaced atoms.[39] The virtues of describing the effects of atomic displacements in terms of the numerical variation of matrix elements of the Hamiltonian evaluated with localized orbitals that move with the atoms was apparently first pointed out by Fröhlich *et al.*[44] and emphasized later by Mitra[45] and by Barisic *et al.*[46] The importance of treating the normalization matrix in the same way has been discussed by Varma *et al.*[47] References 44–47 are concerned with electron-phonon coupling.

IV. ADSPACES: INTERSTITIALS AND CHEMISORPTION

In the preceding section we considered systems characterized by perturbations that alter quantitative aspects of the underlying atomic states, but leave the *number* of states unchanged. Examples of such perturbations are substitutional impurities (of the same chemical type as the host) and displaced atoms. In this section we introduce the extension of the formalism required for the description of systems in which the number of atomic states is *increased* in a fundamental way. In other words, we are concerned here with systems in which the perturbation introduces atomic states for which there is no natural analog in the unperturbed system. Interstitial impurities and atoms chemisorbed on a crystal surface are examples of this type of perturbation, but perhaps the simplest example is that of a substitutional transition-metal impurity in a non-transition-metal host. We will therefore discuss the required extension of the formalism as it would be applied to the transition-metal-impurity problem, but we ask the reader to keep in mind that the basic idea applies to a variety of problems.

The significance in the present context of a transition-metal impurity in a non-transition-metal host is that, while we can regard the *s* and *p* states of the transition metal as perturbed versions of the *s* and *p* states of the host, there is nothing in the unperturbed system that corresponds to the *d* states. In the differential-operator approach to this type of problem we are obliged to synthesize the new *d* states out of the high-energy states of the host. While this is mathematically possible it is certainly not incisive and the price that must be paid in computational effort, when this route is followed, is considerable.[31] It is this type of problem that leads to a discussion of the number of high-energy states (bands) of the host that must be included in an accurate description of the impurity system. As Lindefelt and Zunger[31] have correctly emphasized, merely representing the Green's function in a basis set that contains the new states does *not* eliminate the need for high-energy states[48] of the unperturbed Hamiltonian in the traditional (differential-operator) approach. In the matrix approach the unperturbed Hamiltonian *matrix* has relatively few excited eigenstates, far too few in general to represent a fundamentally new atomic state. The adspace idea, which we now describe, permits us to introduce the additional atomic states directly.

Our approach to this type of problem follows from the demand that the basis-set expansion in Eq. (3) be the only approximation made in the solution of the single-particle equations. The fact that the matrices of the perturbed problem have a greater dimension than those of the unperturbed problem is accommodated by adding additional rows and columns to the matrices of the unperturbed system. For the illustrative example of the transition-metal impurity, the matrix denoted in the preceding section by $\epsilon S^0 - H^0$ is replaced by $\epsilon\tilde{S}^0-\tilde{H}^0$, with

$$\epsilon\tilde{S}^0-\tilde{H}^0 \equiv \begin{bmatrix} (\epsilon-\epsilon_d)\delta_{dd'} & 0 \\ 0 & \epsilon S^0-H^0 \end{bmatrix}, \tag{22}$$

where $S^0_{\nu\nu'}$ and $H^0_{\nu\nu'}$ are the normalization and Hamiltonian matrices of the host crystal [Eqs. (5) and (7)] and the index d denotes the d states. We can think of ϵ_d as the energy of the atomic d state, but it is quite arbitrary,[49] because whatever we put in the dd' block of $\tilde{S}^0$ and $\tilde{H}^0$ is removed when we construct the dd' block of the difference matrices δS and δH. The crucial property of $\epsilon\tilde{S}^0-\tilde{H}^0$ is that it be easily invertible to obtain the unperturbed Green's-function matrix for the Dyson equation [Eq. (19)]. We see that the $\epsilon\tilde{S}^0-\tilde{H}^0$ defined in Eq. (22) is in fact easily inverted to obtain

$$\tilde{G}^0(\epsilon)=\begin{bmatrix} \delta_{dd'}/(\epsilon-\epsilon_d) & 0 \\ 0 & G^0(\epsilon) \end{bmatrix}. \tag{23}$$

We emphasize several points in this context. First and foremost, the simple and direct inclusion of new states is only possible in the matrix formulation. In the differential-operator approach the unbounded character of the spectrum of the differential operator implies that the corresponding Green's function contains a complete set of states,[50] which in turn implies that the introduction of any new states, such as the *d* states in our transition-metal example, creates a problem of overcompleteness.[15,20,22,23,51] Our approach is based on the observation that the high-energy portion of the spectrum of the differential operator does not provide a usefully concise description of additional valence states. Working with linear combination of atomic orbitals (LCAO) type Hamiltonians, which contain only low-energy valence states, simultaneously eliminates the problems associated with the high-energy spectrum and permits the direct introduction of additional valence states, as required, by the traditional techniques of quantum chemistry. Second, we point out that the question of how many bands of the host crystal (the unperturbed system) are required for an adequate description of the perturbed system[31] simply does not arise in the matrix formulation. Finally, we emphasize that the adspace idea is not restricted to the particular illustrative example considered above; it is equally applicable to interstitial impurities and it is fundamental to our present efforts to understand molecular chemisorption (see Sec. VII). The application of the adspace idea to the specific problem of transition-metal impurities in semiconductors was discussed by Pantelides and Williams[52] and is also the subject of a planned future paper by Pantelides.[53] Perhaps the best example of the use of a Dyson equation to couple the Green's functions of two independent systems is the treatment of crystal interfaces by Pollmann and Pantelides.[25] (The interface study was performed within the framework of empirical tight-binding theory, for which the problem of overcompleteness does not arise.)

V. REDUCED SPACES: THE "IDEAL" CONCEPT

In the preceding section we considered the application of the matrix-Green's-function approach to a case in which the perturbed system contained *more* atomic states than the unperturbed system. We consider now the important class of problems characterized by the perturbed system possessing *fewer* atomic states than the unperturbed system. This class of problems includes crystal surfaces, vacancies, and voids. In the preceding section we saw that an increase in the fundamental number of states on going to the perturbed system complicates the analysis at the point where the H and S matrices of the perturbed and unperturbed systems are subtracted to form the perturbation matrices $\delta S_{\nu\nu'}$ and $\delta H_{\nu\nu'}$. In contrast with Sec. IV, when the number of basis functions required for the description of the perturbed system is smaller than that required for the unperturbed system, the construction of δH and δS is not complicated. (Some of the elements of $S^0_{\nu\nu'}$ and $H^0_{\nu\nu'}$ are simply not used.) The complication caused by a reduction in the number of states arises when we attempt to proceed from the definition of the Green's-function matrix [Eq. (17)] to the Dyson equation [Eq. (19)] by multiplying by the Green's-function matrix for the unperturbed system. The complication is simply that the quantity we need in order to proceed is not the quantity we know. We know $G^0_{\nu\nu'}(\epsilon)$, the inverse of the *entire* matrix $\epsilon S^0_{\nu\nu'}-H^0_{\nu\nu'}$, whereas what we need is the inverse of just the *portion* of $\epsilon S^0_{\nu\nu'}-H^0_{\nu\nu'}$ used in the construction of $\delta H_{\nu\nu'}$ and $\delta S_{\nu\nu'}$. For the present discussion let us refer to the matrix $\epsilon S^0_{\nu\nu'}-H^0_{\nu\nu'}$ as A, and to the unperturbed Green's-function matrix $G^0_{\nu\nu'}(\epsilon)$ as B. In this notation Eq. (18) becomes simply

$$\begin{bmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{bmatrix} \begin{bmatrix} B_{11} & B_{12} \\ B_{21} & B_{22} \end{bmatrix} = \begin{bmatrix} 1_{11} & 0 \\ 0 & 1_{22} \end{bmatrix}, \tag{24}$$

where 1 refers to the subset of the $\{\nu\}$ indices used in the description of *both* the perturbed and unperturbed systems, while 2 refers to the subset of the $\{\nu\}$ indices used *only* in the description of the unperturbed system. For example, in describing a vacancy the indices labeled 2 refer to the atom that was removed to form the vacancy. We obtain what we need, the inverse of A_{11}, from what we know, the entire B matrix, by regarding Eq. (24) as four equations and combining two of the four,

$$A_{11}B_{11}+A_{12}B_{21}=1_{11}\,, \tag{25a}$$

$$A_{11}B_{12}+A_{12}B_{22}=0\,, \tag{25b}$$

by solving Eq. (25b) for A_{12} and substituting the result into Eq. (25a) to obtain[54]

$$A_{11}(B_{11}-B_{12}B_{22}^{-1}B_{21})=1_{11}\,. \tag{26}$$

We identify the quantity in parentheses as the desired inverse $\epsilon S^0_{\nu\nu'}-H^0_{\nu\nu'}$ in the reduced space. This quantity is called the "ideal" Green's-function matrix $G^I_{\nu\nu'}(\epsilon)$. [We remind the reader that the individual quantities (e.g., B_{22}) appearing in Eqs. (24)–(26) are matrices.] For any Green's-function matrix G, its ideal counterpart G^I is given by

$$G^I \equiv G_{11}-G_{12}G_{22}^{-1}G_{21}\,, \tag{27}$$

where 1 and 2 refer to a partitioning that describes the removal of some of the functions contained in the expansion set $\{\varphi_\nu(\vec{r})\}$.

There is one remaining aspect of the ideal construction that we wish to clarify. Equation (27) appears to suggest that the calculation of the ideal Green's function requires the inversion of a matrix G_{22}, which in the case of surface problems, for example, would have infinite dimension. Recall that the subset of indices indicated by 2 in Eqs. (24)–(27) is the subset corresponding to atomic sites that are present in the unperturbed problem, but not present in the perturbed problem. In constructing the ideal Green's function for a surface, for example, the 2 in Eqs. (24)–(27) refers to the *infinite* set of atomic sites located in the vacuum region of the perturbed problem. The inversion of an infinite portion of $G^0_{\nu\nu'}$ for a geometry such as a surface would indeed represent a serious obstacle for this development, if it were, in fact, necessary. What makes the required inversion of G_{22} tractable is the restricted range of the matrix $\epsilon S^0_{\nu\nu'} - H^0_{\nu\nu'}$, which, in turn, is a direct result of the restricted spatial range of the expansion set $\{\varphi_\nu(\vec{r})\}$. The range of $\epsilon S^0_{\nu\nu'} - H^0_{\nu\nu'}$ enters the development at the point where we solve Eq. (25b) for A_{12}. The essential observation here is that the elements of the matrix A_{12} are significant in magnitude only for a small subset of the 2 indices. If we denote this subset of the 2 indices by 3 and the remaining 2 indices by 4 then Eqs. (25) can be rewritten

$$A_{11}B_{11} + A_{13}B_{31} = 1_{11} , \tag{28a}$$

$$A_{11}B_{13} + A_{13}B_{33} = 0 , \tag{28b}$$

$$A_{11}B_{14} + A_{13}B_{34} = 0 . \tag{28c}$$

We see in this way that, although the matrix elements in Eq. (28c) are not negligible, this equation is irrelevant to the construction of the ideal Green's-function matrix. We can solve Eq. (28b) for A_{13}, substituting the result into (28a) to obtain the Dyson-type equation [Eq. (27)] for the ideal Green's-function matrix. In other words only a small portion of the unperturbed Green's-function matrix (B_{33}) must be inverted to obtain the ideal Green's-function matrix. For example, if all interatomic interactions other than those between nearest neighbors are assumed negligible, then the ideal Green's-function matrix describing the surface of a group-IV semiconductor, such as Si, requires only the inversion of 4×4 matrices.[25]

The ideal Green's function is very useful as both a conceptual and a calculational tool. Its utility as a calculational tool has already been demonstrated[24,25] in applications of empirical tight-binding theory. In the context of self-consistent-field calculations it plays the additional role of permitting us to decompose the total effect on the electronic structure of removing one or more atoms into two conceptually different components. The ideal Green's-function matrix itself describes the "topological" component of the total effect, that is, the effect on the state density, etc., of prohibiting propagation through one or more atomic sites. The remaining component of the total change, that is, the effect of letting the electron gas self-consistently respond (relax) to the removal of the atom(s), is calculated with the use of the ideal Green's-function matrix. As described for the specific case of molecular chemisorption below (Sec. VII), this "relaxation" component of the total change in the electronic structure is given by a Dyson equation in which the ideal Green's function plays the role of the unperturbed Green's function, and the "scattering potential" is that due to the response of the electron gas to the removal of atom(s). The ideal construction therefore makes it possible to examine separately and directly the two components of the total effect. The work of Pantelides and co-workers on semiconductor defects[24,27] and surfaces[25] establishes the important empirical fact that the electronic-relaxation component of the total change is often only a small fraction of the total effect.

The fundamental result of the ideal concept, Eq. (27), was derived by Pantelides and co-workers[24,25] in the context of empirical tight-binding theory, with the use of physical ideas such as bond cutting and infinite atomic orbital energies. Subsequently, the validity of the ideal concept was unfortunately thrown into question.[55] We feel that the purely mathematical derivation provided above, together with the discussion of the topological and relaxation components of the total effect, makes both the content and the validity of the ideal construction completely unambiguous.

VI. SIMPLIFIED SUMMATION OVER THE OCCUPIED STATES

In this section we describe a procedure that substantially simplifies the evaluation of the density matrix $\rho_{\nu\nu'}$. We remind the reader that the density matrix is the fundamental quantity required for the evaluation of the electron density and the total energy. The procedure consists of the straightforward numerical approximation of the contour integral in Eq. (14). The unperturbed Green's-function matrix

$G^0_{\nu\nu'}(z)$ is constructed for a set of complex values of z lying on a convenient contour; the Dyson equation is then used to obtain the perturbed Green's-function matrix $G_{\nu\nu'}(z)$ for the same set of z values, and finally, Eq. (14) is approximated by a properly weighted sum over the z values. As mentioned above the integral in Eq. (14) has usually been performed by collapsing the contour to the real axis. Integrating along the real axis is difficult because the Green's function almost always varies extremely rapidly with energy,[25] so that an accurate evaluation of the integral requires a knowledge of $G_{\nu\nu'}(\epsilon)$ on a very fine mesh of ϵ values. A special example of the rapid variation of the Green's function warrants comment. When the perturbation produces discrete states (surface states, e.g.) in the gaps of the spectrum of the unperturbed Hamiltonian, the contribution of such states to integrated properties, such as the electron density, must be properly included. In the usual procedure of integrating along the real axis the existence and precise energy position of such states must be determined by techniques (e.g., root finding[27]) that are essentially unrelated to the rest of the calculation. When the contour is displaced away from the real axis these states lose their discrete character and are automatically included *without their explicit construction.*

The crucial fact underlying the procedure we recommend is provided by Eq. (12), which indicates that the only aspect of the very complicated ϵ dependence of the Green's function that is relevant to the construction of the density matrix is the distinction between occupied and unoccupied states. In other words, the contour integration in Eq. (14) is nothing more than a particular representation of the Heaviside step function $\Theta(\epsilon_F-\epsilon_i)$ appearing in Eq. (12):

$$\Theta(\epsilon_F-\epsilon_i)=\frac{1}{2\pi i}\int_{C(\epsilon_F)}\frac{dz}{z-\epsilon_i}\ , \tag{29}$$

where the notation $C(\epsilon_F)$ indicates that the only requirement of the contour is that it enclose the ϵ_i below the Fermi level. The contour therefore cuts through the real axis at ϵ_F. For example, the contour can be taken to be a rectangle enclosing the occupied states. A special case of this type of contour consists of expanding the rectangle so that three of its sides lie at infinity, with the fourth side of the rectangle consisting of the vertical line passing through the real axis at ϵ_F.[56] Each of these choices of contour has its own numerical advantages and disadvantages.[57] All such choices share the virtue of requiring relatively few evaluations of the perturbed and unperturbed Green's-function matrices, and they all share the disadvantage of providing a much less detailed picture of state-density changes than that provided by contour choices lying on or near the real axis. The density of points along the contour used in the numerical approximation of the contour integral [Eq. (29)] can be identified with the temperature in the finite-temperature Green's-function formalism.[58] The numerical approximation to the contour integral therefore has the operational effect of thermally smearing the Fermi-occupation function (the greater the numerical precision, the lower the temperature).

VII. AN EXAMPLE: CHEMISORBED MOLECULES

In this section we briefly describe an example of how the ideas of the previous sections can be combined to solve a problem of current interest. The problem in question is the chemisorption of molecules on a solid surface, and the approach to this problem that we now summarize is the one we are pursuing with detailed numerical calculations. Our formulation of the problem consists of several almost independent steps. In the first step we describe the formation of the free molecule from free atoms. (For illustrative purposes, we consider a diatomic molecule composed of atoms a and b.) Using the adspace notion of Sec. IV, we form the Green's-function matrix $G^A(z_i)$ representing the noninteracting free atoms,

$$G^A(z_i)=\begin{bmatrix}\delta_{aa'}/(z_i-\epsilon_a) & 0\\ 0 & \delta_{bb'}/(z_i-\epsilon_b)\end{bmatrix}\ , \tag{30}$$

where a and b denote the states of the two atoms and z_i is a particular point on the contour in Eq. (14). A Dyson equation in which the free-atom Green's function $G^A(z_i)$ plays the role of the unperturbed Green's function is then used to construct the Green's function $G^M(z_i)$ for the free molecule:

$$G^M(z_i)=G^A(z_i)+G^A(z_i)(\delta H-z_i\delta S)G^M(z_i)\ . \tag{31}$$

Note that, just as in Sec. IV, the definition of $G^A(z_i)$ is largely a matter of convenience,[49] because whatever description of the free atom is used for $G^A(z_i)$ is subtracted out in the construction of δH and δS. Since the solution of the Dyson equation is exact (not perturbative) we are not obliged to make $G^A(z_i)$ particularly realistic. The detailed description of both the individual atoms and the coupling between them is carried by δH and δS.

We now turn to the substrate half of the problem. Starting with the Green's-function matrix for the bulk perfect-crystal substrate $G^B(z_i)$, we form the ideal Green's-function matrix $G^I(z_i)$ for the surface with the use of Eq. (27). That is,

$$G_{RR}^I = G_{RR}^B - G_{RL}^B (G_{LL}^B)^{-1} G_{LR}^B \ , \tag{32}$$

where the partitioning labels L and R are intended to suggest the left and right half-spaces of the bulk. The relaxation of the electron gas at the surface of the substrate is then described by a second Dyson equation in which the ideal-surface Green's-function matrix G^I plays the role of the unperturbed Green's function,

$$G^S(z_i) = G^I(z_i) + G^I(z_i)\delta H' G^S(z_i) \ . \tag{33}$$

The quantity $\delta H'$ appearing in Eq. (33) is the change in the Hamiltonian matrix associated with the electronic relaxation at the bare surface, and $G^S(z_i)$ is the full bare-surface Green's-function matrix (including electronic relaxation).

The chemisorption process itself is represented by a final Dyson equation that describes the interaction between the free molecule and the bare surface. In this Dyson equation the role of the unperturbed Green's function is played by $G^{MS}(z_i)$, which describes the free molecule and the bare surface and is formed by again using the adspace concept of Sec. IV,

$$G^{MS}(z_i) = \begin{bmatrix} G^M(z_i) & 0 \\ 0 & G^S(z_i) \end{bmatrix} . \tag{34}$$

Note that the $G^M(z_i)$ and the $G^S(z_i)$ appearing in Eq. (34) are the solutions of Eqs. (31) and (33). The Dyson equation describing the molecule-surface interaction relates the full Green's-function matrix $G(z_i)$ to $G^{MS}(z_i)$,

$$G(z_i) = G^{MS}(z_i) + G^{MS}(z_i)(\delta H'' - z_i \delta S'')G(z_i) \ . \tag{35}$$

The matrices $\delta H''$ and $\delta S''$ describe both the coupling of the molecule and the substrate and the changes in the molecule and the surface that result from the new coupling. Equations (31), (33), and (35) refer implicitly to self-consistent-field iterations, for which the required electron density is constructed by summing the contributions from the z_i (see Sec. VI). We have presented Eq. (33) without a contribution from the change in the normalization matrix δS in order to exhibit the implication of the surface atoms retaining their bulk positions; the surface atoms will in general relax and reconstruct, in which case a contribution from δS will be present.

VIII. SUMMARY AND DISCUSSION

Much of what we have described above can be summarized by the observation that our formalism makes available to the detailed self-consistent-field calculations required by density-functional theory many of the attractive features of empirical tight-binding theory. Since the latter never considers anything beyond matrix elements of the Hamiltonian in a unspecified LCAO basis set, it is, by construction, an example of the matrix approach. For example, within tight-binding theory the description of displaced atoms is automatically the one we advocate. Another useful summary of the approach described above is that it is based entirely on a *single* approximation, the expansion of the wave function in a basis set of atomiclike (localized) functions [Eq. (3)]. Furthermore, the single approximation is one that has been widely tested[32,59–64] and for which there is considerable chemical intuition and lore.

The adspace idea, which allows us to study directly the interaction between constituents of complicated systems, such as chemisorbed molecules and transition-metal impurities in *s* and *p*-bonded hosts, has a long history and an extensive literature.[15,20,22,23,65–67] The Anderson model of dilute impurities[68] is perhaps its most renowned ancestor. Once again, the idea is a natural one within the framework of tight-binding theory.[25,52,67] In the context of theories employing differential operators and single-particle potentials, previous work[15,20,22,23,51] of which we are aware has taken the eigenvalue spectrum of the host to be unbounded, with the result that the introduction of new states (e.g., those of the molecule or the *d* states of the transition metal) creates a problem of overcompleteness.[50,51] The work of Kanamori *et al.*,[15] that of Grimley,[20,23,51] and that of Gunnarsson and Hjelmberg,[22] for example, is focused on the correct treatment of this overcompleteness. Another unfortunate manifestation of the unbounded spectrum of the differential operator is the difficulty associated with the determination of the real part of the unperturbed Green's function. Although these difficulties have been successfully dealt with[27,29,48] in various levels of approximation, it seems fair to say that both the problems associated with the unbounded spectrum and the solutions to these problems introduce quantities and concepts with rather little chemical and physical appeal. The principal motivation for the use of the differential-operator Green's function is that it is the most natural embodiment of a nearly-free-electron host or substrate. The work of Singhal and Callaway[60] on Al, the prototype of nearly-free-electron materials, has clearly demonstrated, however, that these systems can be accurately described with the use of localized atomic functions.

The ideal construction plays a particularly important role in the study of systems, such as surfaces, in which the difference in spatial extent between the perturbed and unperturbed systems is either large or infinite. Without the ideal construction for such systems we are forced to rely on some form of matching. Matching of the wave function itself[14,26,30] has the disadvantage of requiring very detailed information about the wave function in regions where we know it least well. Application of the matching idea to matrices leads to the transfer-matrix concept, which has been used[69] to study tight-binding models of surfaces.

The combined use of the adspace idea and the ideal construction makes it possible to treat geometrical arrangements of atoms that possess no convenient overall shape (e.g., spherical[36] or planar[32–34]). Molecular chemisorption is an example of such a geometry. Combining the ideal and adspace ideas also permits the implementation of a treatment of chemisorption discussed by Grimley, that of the "defective" solid.[23] The idea is to perform detailed calculations for a molecular cluster consisting of a chemisorbed atom (or molecule) and a small subset of the substrate atoms. The coupling of this cluster to the defective solid (the remaining atoms of the substrate) is then considered as a separate step. The adspace and ideal concepts of Secs. IV and V permit this procedure to be carried out without approximation. The defective-solid idea can be viewed as a difficult decomposition of the chemisorption process than that considered in Sec. VII. Viewing a substitutional impurity as a free atom interacting with a vacancy, as Scheffler and Pantelides[38] have done, exemplifies the same underlying idea.

The contour-integration technique we use to construct the density matrix makes the calculation interestingly similar to density-matrix methods.[70] In these methods individual electronic states of the system are not explicitly constructed. Rather, the total-energy functional is minimized with respect to the elements of the density matrix. The nonlinear variation required for this minimization is complicated and has been carried out only for relatively simple systems.

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[*] Permanent address: Sandia Laboratories, Albuquerque, NM 87185, a Department of Energy facility.

[1] W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965).

[2] A. R. Williams and U. von Barth, in *The Theory of the Inhomogeneous Electron Gas,* edited by N. H. March and S. Lundqvist (Plenum, New York, in press).

[3] O. Gunnarsson, J. Harris, and R. O. Jones, J. Chem. Phys. 67, 3970 (1977).

[4] B. I. Dunlap, J. W. D. Connolly, and J. R. Sabin, J. Chem. Phys. 71, 4993 (1979).

[5] V. L. Moruzzi, J. F. Janak, and A. R. Williams, *Calculated Electronic Properties of Metals* (Pergamon, New York, 1978).

[6] M. Yin and M. L. Cohen, Phys. Rev. Lett. 45, 1004 (1980).

[7] N. D. Lang and A. R. Williams, Phys. Rev. 18, 616 (1978).

[8] O. Gunnarsson, H. Hjelmberg, and B. I. Lundqvist, Phys. Rev. Lett. 32, 292 (1976); Surf. Sci. 63, 348 (1977).

[9] C. M. Varma and A. J. Wilson, Phys. Rev. B 22, 3795 (1980).

[10] N. D. Lang, Phys. Rev. Lett. 46, 842 (1981).

[11] G. F. Koster and J. C. Slater, Phys. Rev. 95, 1167 (1954).

[12] J. Callaway, J. Math. Phys. 5, 783 (1964).

[13] J. Koutecky, Adv. Chem. Phys. 9, 85 (1965).

[14] F. Garcia-Moliner and J. Rubio, J. Phys. C 2, 1789 (1969).

[15] J. Kanamori, K. Terakura, and K. Yamada, Prog. Theor. Phys. 41, 1426 (1969); *ibid.* Suppl. 46, 221 (1970).

[16] F. Bassani, G. Iadonisi, and B. Preziosi, Phys. Rev. 186, 735 (1969); M. Jaros and J. Brand, Phys. Rev. B 14, 4494 (1976).

[17] D. Kalkstein and P. Soven, Surf. Sci. 26, 85 (1971).

[18] P. Lloyd and P. V. Smith, Adv. Phys. 21, 69 (1972).

[19] D. W. Bullett, R. Haydock, V. Heine, and M. J. Kelley, in *Solid State Physics,* edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1980), Vol. 35.

[20] T. B. Grimley, in *1973 Varenna Summer School on the Dynamic Aspects of Surface Physics,* edited by F. O. Goodman (Editrice Compositori, Bologna, 1974).

[21] A. van der Avoird, S. P. Liebmann, and D. J. M. Fassaert, Phys. Rev. 10, 1230 (1974).

[22] O. Gunnarsson and H. Hjelmberg, Phys. Scr. 11, 97 (1975).

[23] T. B. Grimley, in *Electronic Structure and Reactivity of Metal Surfaces,* edited by E. G. Derouane and A. A. Lucas (Plenum, New York, 1976).

[24] J. Bernholc and S. T. Pantelides, Phys. Rev. B 18, 1780 (1978).

[25] J. Pollmann and S. T. Pantelides, Phys. Rev. B 18, 5524 (1978).

[26] R. E. Allen, Phys. Rev. B 19, 917 (1979).

[27] J. Bernholc, N. O. Lipari, and S. T. Pantelides, Phys. Rev. Lett. 41, 977 (1978); Phys. Rev. B 21, 3545 (1980).

[28] G. A. Baraff and M. Schlüter, Phys. Rev. Lett. 41, 892 (1978); Phys. Rev. B 19, 4965 (1979).

[29] P. H. Dederichs and R. Zeller, in *Advances in Solid State Physics,* edited by J. Treusch (Vieweg, Braunschweig, 1981), Vol. XXI, p. 243.

[30] J. E. Inglesfield, J. Phys. C 14, 3795 (1981).

[31] U. Lindefelt and A. Zunger, Phys. Rev. B 24, 5913 (1981).

[32] P. J. Feibelman, J. A. Appelbaum, and D. R. Hamann, Phys. Rev. B 20, 1433 (1979).

[33] S. G. Louie, Phys. Rev. Lett. 42, 476 (1979).

[34] M. Posternak, H. Krakauer, and A. J. Freeman, Phys. Rev. B 21, 5601 (1980).

[35] G. D. Watkins and R. P. Messmer, Phys. Rev. Lett. 25, 656 (1970); Phys. Rev. B 7, 2568 (1978).

[36] K. H. Johnson, Adv. Quantum Chem. 7, 143 (1973).

[37] S. G. Louie, M. Schlüter, J. R. Chelikowsky, and M. L. Cohen, Phys. Rev. B 13, 1654 (1976).

[38] M. Scheffler and S. T. Pantelides (unpublished).

[39] G. A. Baraff, E. O. Kane, and M. Schlüter, Phys. Rev. B 21, 5662 (1980).

[40] G. A. Baraff, E. O. Kane, and M. Schlüter, Phys. Rev. B 25, 548 (1982).

[41] Approximations are, of course, inevitable in any numerical calculation. We are trying to distinguish here approximations of formal character, such as the approximation of the high-energy spectrum of the Hamiltonian by that of a free particle.

[42] H. P. Hjalmarson, P. Vogl, D. J. Wolford, and J. D. Dow, Phys. Rev. Lett. 44, 810 (1980).

[43] D. R. Hamann, M. Schlüter, and C. Chiang, Phys. Rev. Lett. 43, 1494 (1979).

[44] H. Fröhlich, S. Machlup, and T. K. Mitra, Phys. Kondens. Mater. 1, 359 (1963).

[45] T. K. Mitra, J. Phys. C 2, 52 (1969).

[46] S. Barisic, J. Labbé, and J. Friedel, Phys. Rev. Lett. 25, 919 (1970).

[47] C. M. Varma, E. I. Blount, P. Vashista, and W. Weber, Phys. Rev. B 19, 6130 (1979).

[48] H. Hjelmberg [Phys. Scr. 18, 481 (1978)] found it necessary to include states 100 − 200 Ry above the vacuum level in his description of chemisorbed *hydrogen.*

[49] From a practical point of view the numerical value of ϵ_d becomes significant if, in an effort to maximize the cancellation of systematic numerical errors, we represent the unperturbed electron density using the same contour integral (see Sec. V) as is used for the perturbed problem. In this case the fact the ϵ_F is fixed by the host means that ϵ_d controls the charge on the unperturbed impurity.

[50] T. D. Lee, *Particle Physics and Introduction to Field Theory* (Harwood, New York, 1981), p. 12.

[51] T. B. Grimley and C. J. P. Newton, Phys. Lett. 51A, 267 (1975).

[52] The virtues of describing transition-metal impurities in terms of the coupling between a free-atom Green's function and the Green's function of the host were discussed by S. T. Pantelides and A. R. Williams in a contributed paper at the Third "Lund" International Conference on Deep-Level Impurities in Semiconductors, May, 1981 (unpublished).

[53] S. T. Pantelides (unpublished).

[54] A. Ralston, *A First Course in Numerical Analysis* (McGraw-Hill, New York, 1965), p. 447.

[55] The utility of the ideal construction has recently been challenged [J. B. Krieger and P. M. Laufer, Phys. Rev. B 23, 4063, (1981)] on the basis of a calculation in which the content of the construction was obscured by formal manipulation. A hole (vacancy) was first created in a medium described by a limited basis set. The hole was then unwittingly *refilled* by allowing new basis functions to replace those that had been removed by the original ideal construction. It was then claimed that the results of the ideal construction (the implications of the hole) are not stable with respect to improvements in the basis set.

[56] W. Kohn and L. J. Sham, Phys. Rev. 137, A1697 (1965); C. Koenig, J. Phys. F 3, 1497 (1973); H. Dreysse and R. Riedinger, J. Phys. (Paris) 42, 437 (1981).

[57] Portions of the contour lying at infinity can be treated analytically, requiring in general a cancellation in the total contour integral of results obtained analytically with those obtained numerically. (The portion of the contour near ϵ_F introduces a function with equal amplitude, but opposite sign, above and below ϵ_F; the remainder of the contour contributes a constant which adds to create the desired step function.) Contour choices in which a portion of the contour lies at infinity also involve large integration weights multiplying small values of the integrand. For these reasons, we prefer contour choices in which all portions of the con-

tour are finite.

[58] A. L. Fetter and J. D. Walecka, *Quantum Theory of Many-Particle Systems* (McGraw-Hill, New York, 1971), p. 248.

[59] E. O. Kane, Phys. Rev. B 13, 3478 (1976).

[60] S. P. Singhal and J. Callaway, Phys. Rev. B 16, 1744 (1977).

[61] J. Callaway, in *Physics of Transition Metals, 1980*, edited by P. Rhodes (IOP, London, 1981), p. 1.

[62] C. S. Wang and B. M. Klein, Phys. Rev. B 24, 3393 (1981).

[63] G. B. Bachelet, H. S. Greenside, G. A. Baraff, and M. Schlüter, Phys. Rev. B 24, 4745 (1981).

[64] B. Delley and D. E. Ellis, J. Chem. Phys. 76, 1949 (1982).

[65] L. Hodges, H. Ehrenreich, and N. D. Lang, Phys. Rev. 152, 505 (1966).

[66] F. M. Mueller, Phys. Rev. 153, 659 (1967).

[67] R. H. Paulson and J. R. Schrieffer, Surf. Sci. 48, 329 (1975).

[68] P. W. Anderson, Phys. Rev. 124, 41 (1961).

[69] L. M. Falicov and F. Yndurain, J. Phys. C 8, 147 (1975).

[70] K.-P. Bohnen and S. C. Ying, Solid State Commun. 30, 301 (1979).