PHYSICAL REVIEW B VOLUME 39, NUMBER 18 15 JUNE 1989-II

Electronic structure of finite or infinite systems in the tight-binding model with overlap

Roland Riedinger, Mustapha Habar, Louise Stauffer, Hugues Dreyssé,
Pierre Léonard,* and Manindra Nath Mukherjee†
Laboratoire de Physique du Solide, Université de Haute-Alsace, 4 rue des Frères Lumière, 68093 Mulhouse CEDEX, France

(Received 10 June 1988; revised manuscript received 27 February 1989)

Much interest is devoted to the study of the electronic structure of defects in bulk and near surfaces and interfaces, with the tight-binding method. Recent progress in this field, namely the concepts of "adspace and subspace," allow a better description of the defects. However, the nonorthogonality of the atomic-orbital basis can no longer be neglected; the overlap matrix has to be considered on the same footing as the Hamiltonian matrix. This is even more crucial in reactive systems, where the overlap and Hamiltonian matrices vary in time, according to the positions of constituent ions. Different representations of specific variance may be built up for an operator; some are more adequate for a given physical property. The recursion method is one of the most powerful methods for computing a finite number of matrix elements of the Green's operator, as continued fractions. We discuss its relationship to variance and we propose a new accurate method for generating the continued fraction which avoids any explicit or implicit usage of the inverse overlap matrix in the molecular case. It provides a new way for doing "quantum-chemistry" calculations even for reactive or diffusive systems. It extends, in principle, to infinite systems, irrespective of the dimension of space. However, numerical problems associated with truncation and convergence remain open in the application made to a nitrogen overlayer adsorbed on chromium.

I. INTRODUCTION

The tight-binding method recently gained the favor of almost all physicists, either as an *ab initio* or as an empirical parametrized model. Bulk band structures and also much more complex systems have been studied; we refer to Ref. 1 for a recent review of the subject. Intense activity has been devoted recently to the study of defects in semiconductors,[2] even near surfaces and interfaces.[3,4] Our research group contributed also to this problem in the metallic case, for the surface segregation of impurities.[5] It has been intensively used by others for chemisorption.[6] The concepts of "adspace and subspace" developed with slight variants by several authors[7–9] are very fruitful, because they allow the treatment of the electronic structure of defects chemically very different to the host. This goal is achieved by an augmented flexible basis set, which allows description on the same footing, the initial system ("pure medium") and the final one ("perturbed medium") within the quantum-mechanics diffusion theory. However, the price to be paid is that the overlap matrix **S** becomes as essential as the Hamiltonian matrix **H** in the formalism; the atomic orbitals can no longer be considered orthogonal. The different representations of a one-electron operator in a nonorthogonal basis, namely the covariant, mixed, and contravariant ones have been clearly analyzed in Ref. 9 for the Green's operator (it is in fact valid for any one-electron operator). In Refs. 9 and 10, the phase-shift description for an isolated impurity in an infinite medium (with or without surfaces and interfaces) has been extended for the variations of the local densities of states when overlap is present. A similar description has been proposed for the chemisorption problem.[6]

Another useful technique in the tight-binding method is the recursion method developed initially by Heine, Haydock, and Kelly (HHK) in a series of papers and reviews.[11–16] It allows computation of a specific matrix element of the Green's operator. It is particularly well adapted to system for which the other approaches fail, either due to the size of the system (molecular calculations when the size of the system grows too much) or to the lack of symmetry (in the case of amorphous systems for instance). Even if HHK examined the nonorthogonal case in Refs. 14 and 17, they did not discuss the variance aspects; their algorithm suffers also from a major shortcoming, i.e., the cutoff in the spatial extension of the inverse overlap matrix; this degrades considerably the usefulness and accuracy of their algorithm.

In a recent contribution, Ballentine and Kollar[18] made the variance aspects for the Green's functions more precise, but they made no significant progress toward the major problem with the inverse of the overlap matrix quoted above. The aim of the present work is to recall some variance aspects for the recursion algorithm, to propose and to test an algorithm which avoids the explicit or implicit use of the inverse overlap matrix $\mathbf{S}^{-1}$ in the recursion method. Therefore, it realizes the goal aimed for by many authors. For a given numerical accuracy $\mathbf{S}^{-1}$ and also $\mathbf{S}^{-1}\mathbf{H}$ have a much greater spatial extension than **S** and **H**; these two have the same extension, and they are usually limited to first or second neighbors.[19] A physical application of the method is devoted to a study of a chromium-nitrogen molecule and to the adsorption of nitrogen on a chromium (001) surface. Other application to amorphous systems, to segregation problems, and to diffusion and catalysis are still in progress.

Our work shows that recursion is a viable alternative for quantum-chemistry calculations. The new developments we present here allow even the consideration of infinite systems. It also constitutes progress in solid-state and surface physics, since we hope to be able to tackle simply and efficiently unsolved problems like heterogeneous catalysis, period effects in the electronic structure of alloys (Ni-Pd for instance), etc.

II. TIGHT-BINDING, IMPURITIES, VARIANCE, AND PHASE SHIFTS

In this section, for the sake of completeness, we recall briefly the tight-binding method with overlap and some recent results for phase shifts of defects in infinite systems. One of the most popular simplified tight-binding models is the extended Debye-Hückel method (EHM),[20] which is widely used by quantum chemists, and also by physicists for the adsorption and other impurity problems for surfaces and interfaces.[21] Even if our method is not restricted at all to EHM, we find it convenient to test in that particular case the new method which we propose. The recursion method may be applied to finite or infinite systems. The finite case is interesting: it allows exact calculations and verifications to be made by the traditional eigenvalue techniques and it allows us to bridge from finite to infinite systems. Thus, the recursion method that we implemented here provides an alternative to quantum-chemistry calculations specially for large or infinite systems. This section, even if it is self-contained, assumes a preliminary knowledge of the various variance representations of an operator, induced by the nonorthogonality of the basis.[9,18] We denote by $\hat{A}$ an abstract operator A in Hilbert space and by $\mathbf{A}$ its matrix representations; the positions of the indices, or an explicit mention, specify its variance. Equations (5), (7), and (23) can be taken as the generic definitions of covariant, contravariant, and mixed representations of an operator. It is easy to check that multiplying by $\mathbf{S}$ lowers an index and multiplying by $\mathbf{S}^{-1}$ raises an index.

The eigenstates $|n\rangle$ of a system are built as a linear combination of atomic orbitals (LCAO) $|a\rangle$; this is a shorthand notation for a spin orbital located at λ, of symmetry m and spin σ:

$$|\alpha\rangle = |\lambda m \sigma\rangle \ , \tag{1}$$

$$|n\rangle = \sum_{\alpha} |\alpha\rangle C_n^{\alpha} \ . \tag{2}$$

C_n^{α} are the expansion coefficients in the LCAO basis. One is led to the eigenvalue problem

$$(E_n \mathbf{S} - \mathbf{H})\mathbf{C}_n = \mathbf{0} \ . \tag{3}$$

$\mathbf{S}$ is the covariant overlap matrix

$$\mathbf{S}_{ab} = \langle a|\hat{1}|b\rangle = \langle a|b\rangle \ , \tag{4}$$

which is Hermitian, positive-definite. $\mathbf{H}$ is the covariant Hermitian Hamiltonian matrix

$$\mathbf{H}_{ab} = \langle a|\hat{H}|b\rangle \tag{5}$$

$\mathbf{C}_n$ is the column vector of complex coefficients defined in (2).

The eigenstates $|n\rangle$ are orthonormal:

$$\langle n'|n\rangle = \delta_{n'n} \ . \tag{6a}$$

By using Eqs. (2) and (4), this is equivalent to

$$\langle n'|n\rangle = \sum_{\alpha,\beta} c_{n'}^{\alpha\dagger} \mathbf{S}_{\alpha\beta} c_n^{\beta} = (\mathbf{c}_{n'}^{\dagger}, \mathbf{S}\mathbf{c}_n) = \delta_{n'n} \ . \tag{6b}$$

In the finite case, from the set of eigenvalues E_n and eigenvectors $\mathbf{C}_n$ of (3), we easily build the contravariant matrix of the Green's operator

$$\hat{G}(z) = (\widehat{z - H})^{-1} = \sum_{\alpha,\beta} |\alpha\rangle \mathbf{G}^{\alpha\beta}(z) \langle\beta| \ . \tag{7}$$

With the definition (2) of Ref. 10 and the spectral representation of operator $\hat{G}$,

$$\hat{G} = \sum_{n} |n\rangle (z - E_n)^{-1} \langle n| \ , \tag{8}$$

we are led to the spectral expression of the contravariant matrix of $\hat{G}$:

$$\mathbf{G}^{\alpha\beta}(z) = \sum_{n} C_n^{\alpha} (z - E_n)^{-1} C_n^{\beta *} \ . \tag{9}$$

The Mulliken population (net charge) $P^{\alpha\beta}$ [Refs. 6(c) and 20] is related to the integral of this element up to the chemical potential

$$P^{\alpha\beta} = -\frac{1}{\pi} \operatorname{Im} \int_{-\infty}^{\mu} G^{\alpha\beta}(E + i0) dE \ , \tag{10}$$

and the electronic charge distribution

$$\rho(\mathbf{r}) = e \sum_{\alpha,\beta} \langle\beta|\mathbf{r}\rangle P^{\alpha\beta} \langle\mathbf{r}|\alpha\rangle \ . \tag{11}$$

These relations have been already established by Grimley and Pisani.[6(b),6(c)]

Their G is indeed the contravariant matrix of Green's operator, which coincides also with the inverse matrix of $(z\mathbf{S} - \mathbf{H})$, in the matrix sense. In the case where the overlap matrix is not unity, the phase-shift derivation for isolated impurities, either substitutional or interstitial, is reported in Refs. 9 and 10 and applied in the case of metals. For metals, the general law of conservation of the electronic charge between the initial and the final state leads to the Friedel sum rule[5,9,10] since the chemical potential is conserved (to order $1/N$) for an isolated impurity in an infinite system. Thus, the value of the phase shift at Fermi energy is prescribed. The variation of the density of states at energy E, $\Delta n(E)$, is related to the derivative of the complex phase shift Z:

$$\Delta n(E) = \lim_{z \to E + i0} \left[\frac{-1}{\pi} \operatorname{Im} \left[\frac{d}{dz} Z(z) \right] \right] \ , \tag{12}$$

with

$$Z(z) = \ln \det[1 + (z\, \Delta\mathbf{S} - \Delta\mathbf{H})\mathbf{G}^{i}(z)] \ . \tag{13}$$

The matrix within square brackets in Eq. (13) is evaluated in the nonorthogonal basis; $\Delta\mathbf{S}$ and $\Delta\mathbf{H}$ are the covariant difference of the overlap and Hamiltonian matrices between the final and initial states. $\mathbf{G}^i$ is the contravariant representation of the Green's operator of the initial state. In the case of localized defects, $\Delta\mathbf{S}$ and $\Delta\mathbf{H}$ are of limited spatial range, and we need to evaluate the corresponding matrix elements of $\mathbf{G}^i$.

In the interstitial or adsorbate case, we recover from Eqs. (12) and (13) the results obtained by Grimley[6(c)] in the case with overlap. The self-energy operator of adatom A is

$$\Delta_{AA'}(z,z') = \sum_{M,M'} (z'\Delta\mathbf{S}_{AM} - \Delta\mathbf{H}_{AM})\mathbf{G}^{1MM'}(z) \times (z'\Delta\mathbf{S}_{M'A'} - \Delta\mathbf{H}_{M'A'}) \ . \tag{14}$$

A denotes the set of orbitals of the adatom, M those of the metallic host. The superscript 1 refers to an intermediate state which incorporates the modification of the overlap and Hamiltonian in the uncoupled subspaces A and M separately.

In Grimley's result, z' coincides with z in formula (14): This is due to the assumption of overcompleteness of the adatom basis with respect to that of the host basis. The self-energy is a second-degree polynomial in z', with matrix coefficients; with evident notation,

$$\Delta(z,z') = (z')^2\Delta_{SS}(z) - z'[\Delta_{SH}(z) + \Delta_{HS}(z)] + \Delta_{HH}(z) \ . \tag{15}$$

The evaluation of various terms in Eq. (15) can be done by recursion: with the states

$$|u_0\rangle = |a\rangle, \quad a \in A \ , \tag{16}$$

$$|v_0\rangle = |\hat{H}a\rangle, \quad a \in A \ , \tag{17}$$

the self-energies can be computed as

$$\Delta_{SH} = \langle u_{0'}|(z - \hat{H}^1_M)^{-1}|v_0\rangle \ , \tag{18a}$$

$$\Delta_{SS} = \langle u_{0'}|(z - \hat{H}^1_M)^{-1}|u_0\rangle \ , \tag{18b}$$

$$\Delta_{HH} = \langle v_{0'}|(z - \hat{H}^1_M)^{-1}|v_0\rangle \ . \tag{18c}$$

III. THE RECURSION METHOD

In this section and in Appendix A, we show that the abstract recursion scheme is unique, even though it may take multiform aspects in various contexts. Only the minimal information necessary for the comprehension of our work is given. The recursion method allows us to describe any matrix element of the Green's operator as a continued fraction.[11–15] The Cambridge group developed also the recursion method in the case of nontrivial overlap for the covariant matrix elements of the Green's operator (implicitly); they did not discuss the variance properties. In the preceding section, it appears that other representations (contravariant, mixed) are sometimes mandatory (for total densities of states or net charges, for instance). A shortcoming of the recursion method exposed in Ref. 14 is that a cutoff must be introduced in the spatial range of the inverse of the overlap matrix $\mathbf{S}^{-1}$, in order to keep the recursion method tractable in infinite systems. But this approximation degrades considerably the numerical accuracy as can be verified for the example of Appendix B. In fact, this cutoff is often hidden by considering effective contravariant Hamiltonian matrices

$$\mathbf{H}^{\text{eff}} = \mathbf{THT} \ , \tag{19}$$

where $\mathbf{T}$ is an approximate truncated inverse overlap matrix. The range of interactions in direct space for the effective Hamiltonian (19) is also greatly enhanced: with $\mathbf{S}$ and $\mathbf{H}$ ranging to first neighbors and $\mathbf{T}$ restricted to first neighbors also, $\mathbf{H}^{\text{eff}}$ will extend up to third neighbors. Therefore the number of levels attainable in the continued fraction by the recursion method will be small, irrespective of the approximation involved in the cutoff of $\mathbf{T}$.

The biorthogonal method reexplored by Ballentine and Kollar[18] suffers from the same drawback: an *ad hoc* short-ranged $\mathbf{S}^{-1}\mathbf{H}$ (mixed representation) makes loose the intrinsic Hermiticity of the problem.[22] The natural extension of the usual recursion method for an initial state $|u_0\rangle$ allows the computation of the matrix element:

$$\langle u_0|\hat{G}(z)|u_0\rangle \tag{20}$$

with the operator $\hat{G}(z)$ defined in (7). The tight-binding system of Eqs. (3) is equivalent to the Schrödinger equation in Dirac's notations:

$$\hat{H}|n\rangle = E_n|n\rangle \ . \tag{21}$$

The action of the Hamiltonian operator $\hat{H}$ on an atomic state $|\alpha\rangle$ is

$$\hat{H}|\alpha\rangle = \sum_{\beta}|\beta\rangle\mathbf{H}^{\beta}{}_{\alpha} \ . \tag{22}$$

$\mathbf{H}^{\beta}{}_{\alpha}$ is the matrix element of $\hat{H}$ in the mixed representation, it verifies

$$\mathbf{H}^{\beta}{}_{\alpha} = \sum_{\gamma}(\mathbf{S}^{-1})^{\beta\gamma}\mathbf{H}_{\gamma\alpha} \ . \tag{23}$$

The usual recursion method extends formally to the nonorthogonal case with overlap: one builds a denumerable set of orthonormal states ($|u_n\rangle$, $n = 0,1,2,\ldots$) from an initial vector $|u_0\rangle$ (and the assumption $|u_{-1}\rangle = 0$) by a two-term recursion:

$$\hat{H}|u_0\rangle = b_{n+1}|u_{n+1}\rangle + a_n|u_n\rangle + b_n|u_{n-1}\rangle \ . \tag{24}$$

a_n, b_n are real coefficients determined by orthogonalization and normalization. The $|u_n\rangle$ are also LCAO's (usually, not eigenstates)

$$|u_n\rangle = \sum_{\alpha}|\alpha\rangle u_n^{\alpha} \ . \tag{25}$$

In the restricted orthonormal subset ($|u_n\rangle$),

$$\langle u_{n'}|u_n\rangle = (\mathbf{u}^{\dagger}_{n'}, \mathbf{S}\mathbf{u}_n) = \delta_{n'n} \ , \tag{26}$$

the Hamiltonian becomes tridiagonal:

$$\mathbf{H}=\begin{bmatrix} a_0 & b_1 & 0 & 0 & \cdots & 0 \\ b_1 & a_1 & b_2 & 0 & \cdots & 0 \\ 0 & b_2 & a_2 & b_3 & \cdots & 0 \\ 0 & 0 & \ddots & \ddots & \ddots & 0 \\ 0 & \cdots & 0 & b_{n-1} & a_{n-1} & b_n \\ 0 & \cdots & 0 & 0 & b_n & a_n \end{bmatrix} . \tag{27}$$

$g_0(z)$ is approximated by the (0,0) element of the inverse matrix of $(z-\mathbf{H})$ [Eq. (27)] as

$$g_0(z)=\mathrm{Adj}(z-\mathbf{H})_{00}/\det(z-\mathbf{H})=\frac{P_1(z)}{P_0(z)} . \tag{28}$$

We refer to Eqs. (38) and (39) for the definition and properties of the P_n polynomials. This leads to a continued-fraction expansion:

$$g_0(z)=[z-a_0-b_1^2 g_1(z)]^{-1} , \tag{29a}$$

with

$$g_p(z)=(z-a_p-b_{p+1}^2 g_{p+1})^{-1}, \quad p=0,1,\ldots . \tag{29b}$$

In Appendix A, we outline the recursion method for generating a set of orthogonal states and for obtaining the associated coefficients (a,b). We recursively apply a Hermitian operator $\hat{A}$ upon an initial state $|u_0\rangle$.

The notion of variance has no precise meaning in the recursion algorithm, since the set of states $(|u_n\rangle)$ is orthonormal. The variance is induced by the choice of the initial state; it is naturally covariant if one chooses for the initial state a specific atomic orbital $|u_0\rangle=|\alpha\rangle$. $g_0(z)$ converges toward the covariant matrix element $\mathbf{G}_{\alpha\alpha}(z)$ as n grows. We have verified numerically in the finite case that for the exact versions of the recursion algorithm (including our new version), $\mathbf{G}_{\alpha\alpha}(z)$ built by recursion coincides with the covariant matrix element built from the spectral representation [cf. Eq. (9)],

$$\mathbf{G}_{\alpha\alpha}(z)=\sum_{\gamma_1,\gamma_2}\mathbf{S}_{\alpha\gamma_1}\mathbf{G}^{\gamma_1\gamma_2}(z)\mathbf{S}_{\gamma_2\alpha} . \tag{30}$$

We can also compute directly with the recursion method a contravariant matrix element $\mathbf{G}^{\alpha\alpha}(z)$: it is sufficient to choose as the initial state

$$|u_0\rangle=\sum_\beta|\beta\rangle(\mathbf{S}^{-1})^{\beta\alpha} \tag{31}$$

(loosely speaking, $\mathbf{S}^{-1}|\alpha\rangle$).

The mixed-representation matrix elements and/or off-diagonal ones may be obtained by the biorthogonal expansion,[17,18] or as a sum of continued fractions by a trick reported by Heine;[13] for instance,

$$\mathbf{G}^{\alpha}{}_{\alpha}(z)=\langle v_0|\hat{G}|u_0\rangle \tag{32a}$$

with

$$|u_0\rangle=|\alpha\rangle , \tag{32b}$$

and $|v_0\rangle$ is as in (31).

The flexibility of the choice of initial state has been used in many circumstances[5(c),23,24] for computing adsorbate self-energies, optical properties, etc.

We test all exact recursion methods presented in Appendix A, as well as our new method for the Hamiltonian, and compared them to the approximate ones, on a chain, in order to test the variance properties (Appendix B). We exhausted the levels for the continued fraction [on this example, the number of levels is equal (or lower in the case of a proper subspace) to the number of atoms in the chain]. Thus the space spanned by $(|u_n\rangle)$ is equivalent to the initial space of atomic orbitals $|\alpha\rangle$ for evaluating the corresponding element of the Green's function. As an exercise, the variance properties and recursion may be verified on a diatomic H_2 molecule described in LCAO formalism with overlap. Then, the eigenvalue problem (2) can be solved by hand and the results can be substituted in the spectral representation of G [Eq. (9)]. Another way is to use any recursion algorithm of Appendix A, for various initial states $|u_0\rangle$. The choice of an eigenstate ($^1\Sigma_g$ or $^1\Sigma_u$) as $|u_0\rangle$ is particularly instructive: the continued fraction has only one level; a_0 is the corresponding eigenvalue and b_1 vanishes (up to numerical rounding errors).

Now we discuss our new method (two-stage recursion), which avoids any implicit or explicit use of $\mathbf{S}^{-1}$ within it. It is well known that the recursion method extracts a finite or denumerable set of orthonormal states $(|u_0\rangle)$ which spans the hull of $(\hat{H}^n|u_0\rangle)$ and which tridiagonalizes the Hamiltonian. Our proposal is to disentangle the generation of the auxiliary orthonormal basis from the Hamiltonian operator $\hat{H}$, which introduces long-ranged $\mathbf{S}^{-1}$ within the algorithm. We therefore build this orthogonal basis with the aid of an auxiliary operator $\hat{A}$ having the same symmetry as $\hat{H}$. The contravariant or the mixed representation of operator $\hat{A}$ has to be as short ranged as possible. We operate $\hat{A}$ onto the initial state $|u_0\rangle$ and we generate a space, which is the hull of $(\hat{A}^n|u_0\rangle)$. For this purpose (first step) we apply the recursion method: we build a set of orthonormal states $|u_0\rangle$ which tridiagonalizes the auxiliary operator $\hat{A}$ with the initial state $|u_0\rangle$. The metric for the coefficients of the expansion in the LCAO basis remains always $\mathbf{S}$. This is a particularly efficient way to extract a subset of orthogonal Löwdin states out of the whole tight-binding manifold. The choice of the auxiliary operator $\hat{A}$, the contravariant representation of which is the identity $\mathbf{I}$ matrix, is often adequate. The corresponding mixed representation of the auxiliary operator is $\mathbf{S}$. This operator is

$$\hat{A}=\sum_{\alpha,\beta}|\alpha\rangle\mathbf{I}_{\alpha\beta}\langle\beta|=\sum_\alpha|\alpha\rangle\langle\alpha| . \tag{33}$$

It should not be confused with the identity operator, which is

$$\hat{I}=\sum_{\alpha,\beta}|\alpha\rangle(\mathbf{S}^{-1})^{\alpha\beta}\langle\beta| . \tag{34}$$

Moreover, the result of operating $\mathbf{S}$ or $\mathbf{S}^{-1}$ onto these states is particularly simple, since they are linear combinations of $\mathbf{S}^n|u_0\rangle$. But we have found pathological cases where the preceding simple choice of the auxiliary operator is insufficient.

(i) In the case of atoms with degenerate orbitals, the generated manifold is not always orthogonal. Sometimes a reorthogonalization with the Gram and Schmidt algorithm[25] overcomes this difficulty.

(ii) A more tricky case is the following: the dimension of the manifold generated by using $\hat{A}$ of Eq. (33) is lower than that obtained with the one-step recursion using operator $\hat{H}$. In this case steps 2 and 3 of our method lead only to approximate results, since the projected Hamiltonian is incomplete. Again, we overcome this difficulty by choosing another auxiliary operator $\hat{A}$ having as a contravariant representation any of **H**, (**SH**+**HS**), **THT**, and **SHS**. All these are more or less short ranged and give an orthogonal basis set with the same dimension obtained with the exact Hamiltonian operator $\hat{H}$. Such operators exist, for instance, an operator $\hat{A}$ such that **H** is its contravariant representation is

$$\hat{A}=\sum_{\alpha,\beta}|\alpha\rangle(\mathbf{H}_{\alpha\beta})\langle\beta| \ . \tag{35}$$

One should forget once the variance attached to the position of the indices of **H** and just consider it as a usual matrix. The covariant matrix of $\hat{A}$ would be **SHS**. We refer to the examples of the next section for the illustration of this discussion.

In the second step, we build the Hamiltonian matrix, which is the projection of the $\hat{H}$ operator onto the orthonormal basis we just generated:

$$\langle u_n|\hat{H}|u_p\rangle=(u_n,\mathbf{H}u_p), \quad 0\le n\le p \ . \tag{36}$$

Only covariant matrix elements of $\hat{H}$ are needed in this step. In this restricted subspace, overlap disappears; it becomes unity [cf. Eq. (26)]. We note that the whole set of vector $|u_n\rangle$ had to be stored for this purpose, and not the two last vectors only (as is usually done in the recursion method).

In the third step, we solve the pseudo-one-dimensional chain problem for the Hamiltonian in the orthonormal basis ($|u_n\rangle$) and this independently of the dimension of the initial space. Direct eigenvalue algorithms (now tractable in this space with reduced dimension) or again the usual recursion method, may be used to solve this step, with the Hamiltonian projected onto the $|u_n\rangle$ states. We discuss the case of recursion. We build a set of orthonormal $|v_n\rangle$ states

$$|v_n\rangle=\sum_{m\ |\le n|}|u_m\rangle v_n^m \ . \tag{37}$$

Since $|u_0\rangle$ is identical with $|v_0\rangle$, we expect from variational arguments that the continued fraction built from the latter chain problem converges toward $\langle u_0|\hat{G}(z)|u_0\rangle$ [Eq. (20)]. This is indeed the case. We checked that our method which *a priori* is only approximate, since derived from variational arguments, is also exact for finite clusters, if the maximal number of levels attained is the same as that obtained with the Hamiltonian $\hat{H}$ with any one-step exact recursion. The main advantage of our method is that the range of interactions can be maintained short ranged in the initial LCAO space (only covariant **H** and/or **S** are used); $\mathbf{S}^{-1}$ is never needed, within the algorithm itself. It may be needed only for building contravariant initial states. The Hamiltonian matrix built according to (36) and used in the second step becomes long ranged, but in a pseudo-one-dimensional chain space only, irrespective of the dimension of the initial space and thus tractable. It extends naturally to infinite systems. We do not discuss here the problem of termination of the continued fraction in the infinite case, since this has been widely discussed elsewhere.[18,26,27] In the next section we compare our method to others in the case of a set of physical problems.

It is also worth mentioning that the approximations of truncation of the Hamiltonian developed by other authors as implementation of the recursion may be used as the first stage of the generation of an orthonormal basis in ours. This is, however, seldom the optimal auxiliary operator.

We discuss now briefly the work of Ballentine and Kollar.[18] This work has the same aim as ours, i.e., to treat systems where overlap cannot be neglected. They introduce a two-side recursion over the mixed representation of the Hamiltonian ($\mathbf{S}^{-1}\mathbf{H}$).

Since they truncate this matrix, they violate the intrinsic Hermiticity of the physical problem (this leads to negative densities of states). We checked that this algorithm with untruncated interactions gives the same results as ours when treated accurately. Special care has to taken with the two-sided recursion; namely, to balance the norms of the two starting vectors $|u_0\rangle$ and $\langle v_0|$ is mandatory, otherwise, the stability is rapidly lost, the $|u_n\rangle$ and $\langle v_n|$ having individual norms that grow and shrink in a complementary way with increasing n, such that $\langle v_n|u_n\rangle=1$. This numerical instability may also lead to negative b_n^2.

The main defect of the work of Ballentine and Kollar[18] is that they do not really solve the problem of the recursion in nonorthogonal bases, since they introduce an *ad hoc* short-ranged Hamiltonian in the mixed representation, following the arguments given by others.[1,28] We checked that $\mathbf{S}^{-1}\mathbf{H}$ built from covariant short-ranged overlap and Hamiltonian are never short ranged. An arbitrarily truncated mixed Hamiltonian makes loose the intrinsic Hermiticity of operator $\hat{H}$, and thus causes unphysical negative densities of states. We recall that our method works quite exactly in that case since we have no such approximation to do at this level.

We recall now some conditions of validity of our method and associated features.

(1) The auxiliary operator $\hat{A}$ operating onto the state $|u_0\rangle$ has to be of the right symmetry for our problem with the shortest interactions possible in its contravariant or mixed representation and has to generate the right manifold of states with the right dimensionality, which span the same space as that created by using the Hamiltonian operator $\hat{H}$ in the exact one-step recursion. The generated states $\hat{A}^n|u_0\rangle$ and thus $|u_n\rangle$ (combinations of the preceding) must be linearly independent. In the trivial case of unit overlap, one recovers the usual recursion method.

(2) For the maximal number of levels (in the case where it is finite), the recursion method provides a subset of exact eigenvalues, but the degenerate eigenvalues appear once only.

We define the $P_n(\lambda)$ polynomials as the determinant of the matrix $\lambda\mathbf{I}-\mathbf{H}$, with the first n columns and rows canceled out [cf. Eqs. (28) and (29)]; the sequence of polynomials (Lanczos spectral method[25])

$$P_{n+1}=1, \quad P_{n+2}=0 , \tag{38}$$

$$P_q(\lambda)=(\lambda-a_q)P_{q+1}(\lambda)-b_q^2P_{q+2}(\lambda) , \quad q=n,n-1,\ldots,0 \tag{39}$$

is a Sturm sequence and thus the roots of $P_n(\lambda)$ are separated. The downward recursion with respect to the index q is particularly well suited to our problem because in one pass we obtain (a) all polynomials $P_q(\lambda)$ needed for evaluating a subset of the spectrum of $\hat{H}$ (the roots λ_i of $P_0(\lambda)=0$ may be obtained from the corresponding Sturm sequence $[P_q(\lambda)]$[29]) and (b) the expression of $g_0(z)$ [Eqs. (28) and (29)] as a rational fraction

$$g_0(z)=P_1(z)/P_0(z) , \tag{40}$$

as well as the spectral representation

$$g_0(z)=\sum_i \frac{\omega_i}{z-\lambda_i} , \tag{41a}$$

with

$$\omega_i=P_1(\lambda_i)/P_0'(\lambda_i) . \tag{41b}$$

The derivatives $P_n'(\lambda)$ may also be obtained by a recurrence relation (involving also P_{n+1}) obtained by deriving (39). We observed a numerical instability in the amplitude of the coefficients ω_i in (41b), while the ratios between the ω_i remain preserved. Therefore we developed a more stable computation of these coefficients combining formal calculus with the evaluation of eigenvalues by Sturm's method.

(3) The set of eigenvalues generated is usually only a subset of the whole manifold. The set of eigenvalues and weights is, however, complete for the initial chosen state $|u_0\rangle$. It gives an accurate Green's-function matrix element $\langle u_0|\hat{G}(z)|u_0\rangle$ which is exact in the finite case for the maximal number of levels of continued fractions and converges with n in the case of truncation or infinite case. Owing to the discrete structure of the spectrum and weights, this convergence has to be studied on the asymptotic values, i.e., the moments.

IV. APPLICATION TO THE CHROMIUM-NITROGEN SYSTEM

In this section, we study the N-Cr system. We chose this system because of our earlier experience with it.[30,31] We perform extended Hückel calculations without self-consistency (it is not the purpose of the present work) and we compare our new spectral method to the more traditional ones, namely direct diagonalization or recursion methods using the full inverse overlap matrix, in the case of finite molecules. As an illustration of the infinite-dimensional case, we compare the calculation of Green's functions in the case of an overlayer of nitrogen on chromium (1×1) N-Cr (001) to the $k_{\parallel}$ calculation of a similar system.[21] The parameters of the calculation are reported in Table I. We present only the local covariant Green's functions on nitrogen. Therefore, the initial states $|u_0\rangle$ are $|\mathrm{N}\ 2\alpha\rangle$, $\alpha=s,p_x,p_y,p_z$.

In the case of the molecule NCr, the total dimension of the tight-binding manifold is 13 (four N orbitals, nine Cr orbitals). We compute the Green's functions either by direct diagonalization, or by the one-step recursion method using the exact Hamiltonian operator; the computation schemes of Appendix A and the biorthogonal version of Ref. 18 with the full inverse of the overlap matrix have been used. Then we verified our new method. We stop the recursion as soon as b_n^2 coefficients become close to zero (this value is seldom exactly reached, due to rounding errors). In this way we obtain a finite number of levels, n, and a finite subspace of dimension n, spanned by n orthonormal vectors generated by the recursion. Going beyond the level for which b_n vanishes approximately would be merely to restart the recursion with a new random initial vector, the noise of rounding errors. Let us discuss in more detail the case of the N $2s$ orbital ($|u_0\rangle=|\mathrm{N}\ 2s\rangle$). The exact versions of the one-step recursion algorithms furnish five levels and independent vectors, whereas our three-step recursion using as auxiliary matrices $\mathbf{I}$, $\mathbf{S}$, or $\mathbf{S}^2$, etc. as contravariant representations of auxiliary operator $\hat{A}$ furnishes only four independent vectors. (This is one of the tricky cases mentioned earlier.) Working with this incomplete subspace would lead to approximate results for the projected Hamiltonian and the recursion coefficients. But using the matrix $\mathbf{H}$ as a contravariant representation of the auxiliary operator $\hat{A}$, or any one mentioned in the preceding section, which are more adequate in the present case, we recover a basis of the right dimensionality and we recover exact coefficients for the continued-fraction coefficients of the equivalent chain problem, while keeping the interactions short ranged in direct space. We analyze according to

TABLE I. Extended Hückel parametrization of the system NCr. A wave function reads $\psi(\mathbf{r})\simeq Y_{lm}(\hat{r})\sum_i a_i r^n \exp(-\zeta_i r)$. This wave function has still to be normalized. bcc chromium lattice parameter is 2.88 Å. In the molecular calculation, the chromium-nitrogen distance is 1.95 Å. In the adsorption problem, the nitrogen atoms sit in the fourfold position, 0.51 (1.95) Å above the first (second) chromium plane. The Hamiltonian is built using the Helmholtz-Wolfsberg formula with $K=1.75$ (Ref. 21).

Orbitals	Energy (eV)	a	ζ (Å^{-1})
N $2s$	-26	1	1.95
N $2p$	-13.4	1	1.95
Cr $4s$	-8.66	1	1.70
Cr $4p$	-5.24	1	1.70
Cr $3d$	-11.20	0.505 79 0.674 72	4.95 1.80

Eqs. (38)–(43) this continued fraction. Using either the Sturm method on the family of polynomials $P_q(x)$ or the direct diagonalization of the tridiagonal representation of $\hat{H}$ in terms of the recursion coefficients (29), we show that the eigenvalues obtained belong to the full spectrum of $\hat{H}$. Moreover, only those associated with eigenvectors having a nonvanishing projection onto $|u_0\rangle$ appear. According to our discussion in Sec. III, degenerate eigenvalues appear only once. The corresponding weight ω_i involves the projection onto $|u_0\rangle$ of the whole degenerate eigenspace associated with the degenerate eigenvalue. These weights coincide with those obtained from the spectral representation

$$G_{00}=\sum_{\gamma,\delta}S_{0\gamma}G^{\gamma\delta}S_{\delta 0}\ , \tag{42}$$

$$\omega_i=\sum_{\gamma,\delta}S_{0\gamma}C_i^{\gamma}C_i^{\delta *}S_{\delta 0}\ . \tag{43}$$

The results are represented in Table II and in Fig. 1.

This detailed example shows the following.

(1) Any exact one-step recursion involving the Hamiltonian operator is an exact alternative to diagonalization for obtaining the spectral properties of the Green's-function matrix elements, for the maximal number of levels (if upper bound, like in the finite molecular systems).

(2) Our method (three-step recursion) avoiding the difficulty of long-ranged $\mathbf{S}^{-1}$ provides also exact results in the molecular case, for an adequate auxiliary operator. But the choice of the auxiliary operator for generating the basis is inductive and requires some imagination. Our method extends naturally to infinite systems, allowing us to tackle problems with chemisorption, reaction paths, heterogeneous catalysis, diffusion barriers, etc. A molecule of finite dimensionality may be used to check the adequacy of the auxiliary operator $\hat{A}$ to generate the basis.

Let us discuss now the infinite-dimensional case, an overstructure of nitrogen on a (001) chromium surface, treated in the extended Hückel model by our new recursion method. We assume that the nitrogen atoms sit in the hollow fourfold sites, above the chromium atoms of the second plane, at the same distance as in the bimolecular system studied above. For the local covariant Green's function, we create the cluster organized into shells around the seed, the nitrogen site.[32]

The various overlap and Hamiltonian matrices needed for all environments are generated and stored. Since the interactions between atoms extend to second neighbors, we used the overlap as an auxiliary matrix in order to build the orthonormal basis in our recursion method. With another choice, the cluster would grow too fast in direct space. Contrary to the molecular case, where it is possible to exhaust the set of states generated from an initial vector, this number of states is usually infinite denumerable, and one has to truncate at a finite rank. The geometrical cluster skeleton of the basis function manifold must consist at least of n shells dressed over the initial seed in the case of the **I** matrix used as a contravariant representation of the auxiliary operator, $2n$ shells in the case of the **H** matrix used in a similar sense, in order to hope to attain n exact coefficients in the continued fraction.

The seed is the set of sites on which the initial wave function has nonvanishing components. We check the orthonormality of the generated basis. We build the projected Hamiltonian and we solve the pseudo-one-dimensional chain problem, again by recursion. We report the corresponding densities of state (spectral weights) in Table III and in Fig. 2 for the nitrogen atom orbitals.

The approximation involved here, with the recursion method with overlap applied to an infinite system, is of the same nature as in the usual recursion method, without overlap. Firstly, the number of shells of the cluster, the number of generated basis vectors with aid of the auxiliary matrix, and the number of levels generated with the one-dimensional chain have to be consistent. The projection of the Hamiltonian onto this truncated basis will also involve an approximation. But this approxima-

TABLE II. Recursion coefficients and related spectral data for the NCr molecule. We report the results for the covariant matrix elements of $\hat{G}$ on nitrogen. The matrix **H** has been used as contravariant representation of the auxiliary operator $\hat{A}$. p_x and p_y orbitals are degenerate and furnish identical results.

	b_{n+1}	a_n	λ_i	ω_i
N 2s	4.488 24	−26.000 00	−26.577 02	0.982 15
	5.080 62	9.911 53	−13.847 34	0.002 37
	3.036 92	−9.634 73	−10.612 94	0.000 60
	1.181 49	−10.534 99	−7.484 21	0.001 68
	0.000 00	−10.582 12	11.681 21	0.013 20
N 2p_x, N 2p_y	1.008 67	−13.400 00	−13.681 02	0.913 97
	2.961 64	−8.694 67	−10.789 50	0.080 57
	0.000 00	−7.259 17	−4.883 33	0.005 46
N 2p_z	2.695 37	−13.400 00	−26.577 02	0.000 71
	8.067 97	8.346 27	−13.847 34	0.937 78
	8.639 43	−12.061 56	−10.612 94	0.039 96
	2.790 99	−20.206 78	−7.484 21	0.011 64
	0.000 00	−9.518 23	11.681 21	0.009 91

tion is also involved in the usual recursion method (without overlap). We did not extrapolate the recursion coefficients here.

Pettifor-Beer's extrapolation,[5(b),5(c),26] linear predictor methods,[27] and Turchi *et al.*'s method adequate in the case of semiconductors[33] may be used. There remains a difficulty: in the three-dimensional case, we encounter still a numerical stability problem, our results giving an

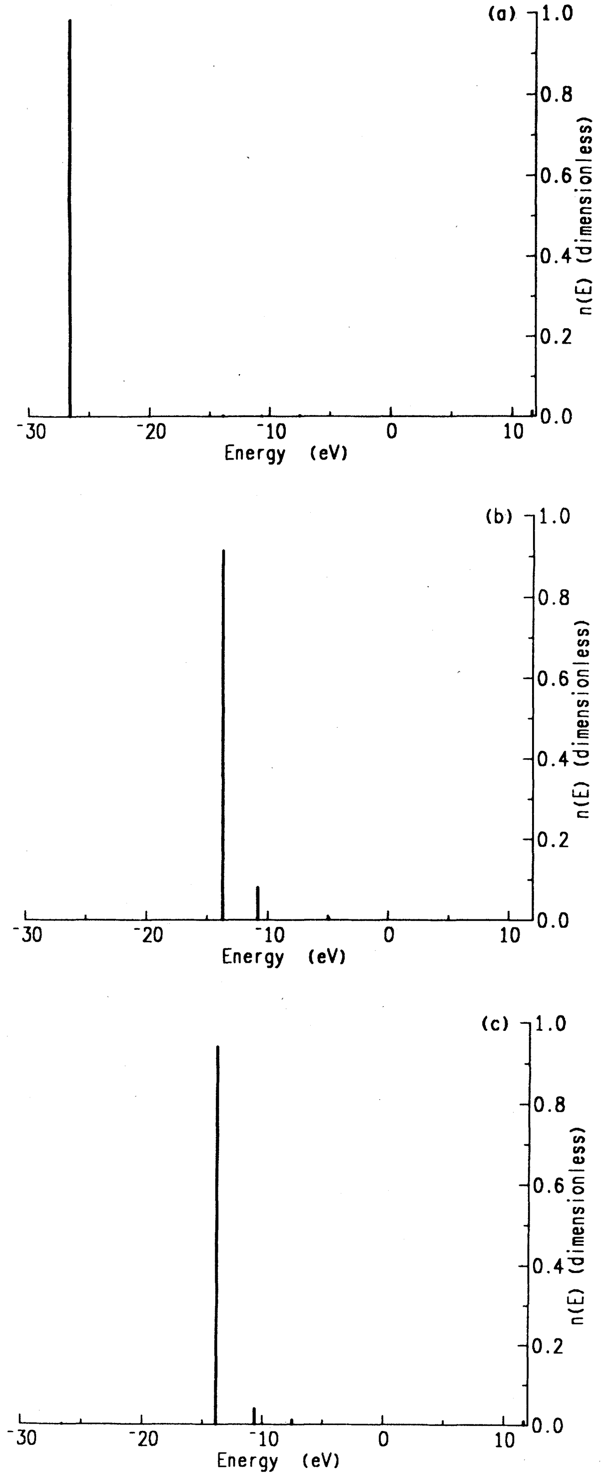

FIG. 1. Density of states (spectral weights) on the N atom orbitals in a NCr molecule. (a) s orbital. (b) p_x,p_y orbitals. (c) p_z orbital.

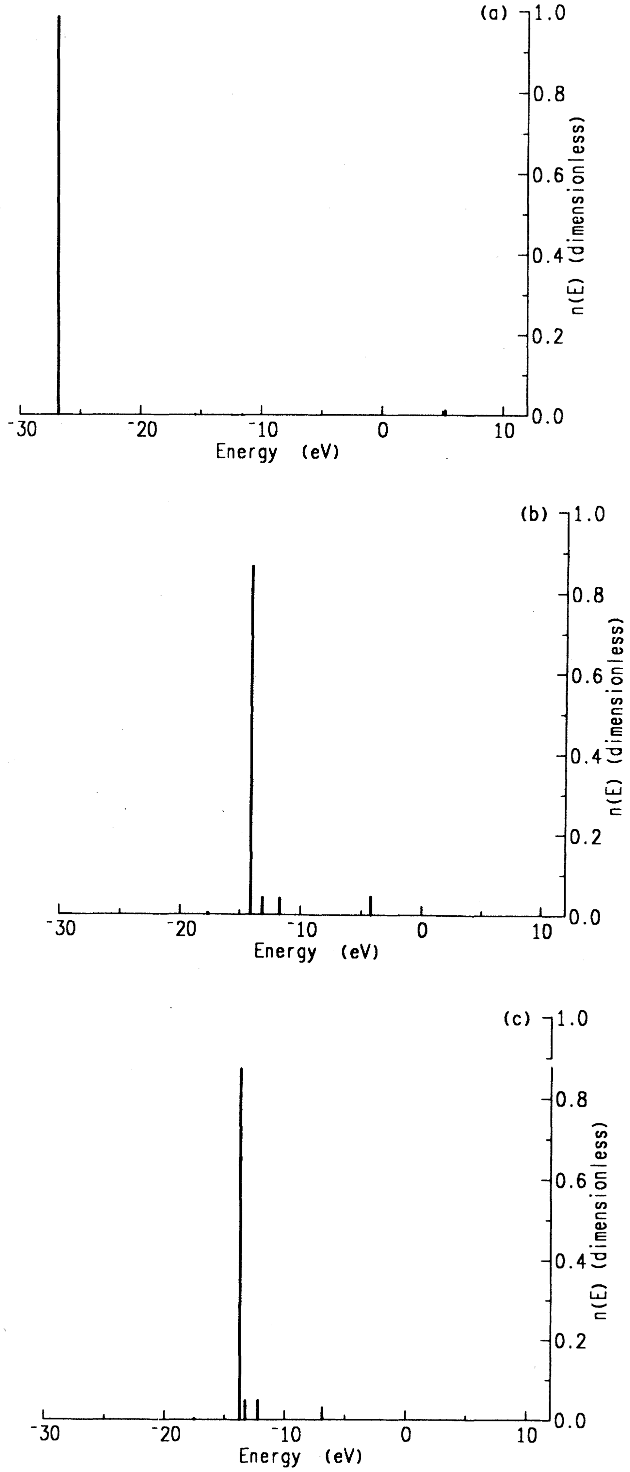

FIG. 2. Density of states (spectral weights) on a N atom in a N(1×1)-Cr(001) overstructure. (a) s orbital. (b) p_x,p_y orbitals. (c) p_z orbital.

TABLE III. Recursion coefficients and associated spectral data for the N atom of N(1×1)-Cr(001) overstructure. The identity matrix has been used as contravariant representation of the auxiliary operator. Six levels of continued fraction and seven shells have been used in the calculation for deriving the diagonal Green's-function covariant matrix elements on a nitrogen atom.

	b_{n+1}	a_n	λ_i	ω_i
N 2s	7.696 78	−26.000 0	−26.808 77	0.983 32
	33.546 14	70.246 80	−15.462 32	0.000 47
	3.550 48	21.346 70	−12.448 46	0.000 24
	1.769 20	−12.367 82	−11.551 80	0.000 67
	0.591 70	−14.135 88	5.246 70	0.011 66
	0.000 00	−12.366 91	87.747 54	0.003 63
N 2p_x, N2p_y	3.028 35	−13.400 00	−17.637 78	0.003 39
	14.179 43	9.355 19	−14.105 89	0.864 40
	3.990 70	7.673 42	−13.109 81	0.042 51
	2.899 50	−13.137 30	−11.690 98	0.041 55
	0.782 88	−15.153 66	−4.196 73	0.044 55
	0.000 00	−13.018 42	23.060 41	0.003 60
N 2p_z	2.256 93	−13.400 00	−17.505 65	0.002 38
	52.060 31	74.633 98	−13.717 10	0.872 46
	2.675 75	24.985 52	−13.263 95	0.047 92
	2.664 29	−14.582 21	−12.193 29	0.047 42
	0.392 05	−14.460 23	−6.885 77	0.029 56
	0.000 00	−13.210 25	107.532 56	0.000 25

eigenvalue expelled to high energy, with a very low weight as the number of levels is increased. We do not run into this difficulty with infinite one-dimensional chains.

The power of the recursion method is that it can be, in principle, applied to any geometry in real space, even to amorphous systems.[34] Let us briefly compare the calculation of a system similar to ours by the $k_\parallel$ method.[21] The contravariant components of the Green's function are the solution of the system

$$\sum_{\gamma}[z\mathbf{S}_{\alpha\gamma}(k_\parallel)-\mathbf{H}_{\alpha\gamma}(k_\parallel)]\mathbf{G}^{\gamma\beta}(k_\parallel,z)=\delta_{\alpha}{}^{\beta}\ . \qquad (44)$$

An alternative evaluation is provided by the spectral method (9). We recall that usually among covariant, mixed, and contravariant representations $\hat{I}$ and $\hat{H}$ are both short ranged in direct space for the covariant one only. The indices α,β,γ refer here to an atom in a given plane parallel to the surface. $A_{\alpha\beta}(k_\parallel)$ refers to a bidimensional Fourier transform of $A_{\alpha\beta}$ parallel to the surface. One obtains the covariant representation in $(k_\parallel)$, with the aid of (37). One has to integrate over an irreducible part of the bidimensional Brillouin zone by analytic methods[35] or sampling over special points.[36] This represents a much larger amount of work, which is restricted to plane geometry only.

V. CONCLUSION

In this paper we showed that the exact recursion methods in the nonorthogonal basis, taking properly into account the overlap matrix, are an exact alternative to quantum-chemistry calculations using diagonalization. Furthermore, the new approach we present here, which distentangles the generation of the recursion basis from the operator $\hat{H}$ itself, overcomes the difficulty of the long-ranged $\mathbf{S}^{-1}$. It represents a major contribution to the recursion method.[37] Combined with other results like the adspace-subspace concepts, it allows us to treat the physics and chemistry of a lot of systems of interest that were not easily tractable earlier. Our variant of the recursion method may be used for quantum chemistry of finite molecular systems as well as, in principle, for infinite-sized ones. The "impurity approach," which allows us to study modifications of the electronic structure in duced by localized defects in an infinite system, needs only a finite amount of work to be done. The application to surfaces and interfaces, even for nonequilibrium situations (diffusion, reactions, and catalysis) is particularly promising.

Our method represents also an original contribution in linear algebra and numerical analysis, for spectral analysis and local inverses of finite and infinite systems which may be useful in other areas, such as the finite-element method. However, the problem of numerical stability and convergence, associated with the truncation in the three-dimensional case, has to be further studied. Other applications of this work to contravariant, mixed, and biorthogonal (nonsymmetric) cases will be presented elsewhere.

ACKNOWLEDGMENTS

The authors wish to thank the Ministère de l'Education Nationale (France) for supporting their work within the project "Calcul Numérique Intensif." Our programs have been implemented on the computer of Centre de Calcul de Strasbourg Cronenbourg (service commun du CNRS). The authors benefited from fruitful discussions and insights on the extended Hückel method with Dr. Dedieu, Dr. M. M. Rohmer (Strasbourg), and Dr. C. Minot (Paris).

APPENDIX A: THE RECURSION ALGORITHM IN A NONORTHOGONAL BASIS

We detail the recursion schemes for a Hermitic operator $\hat{A}$ acting recursively on an initial state $|u_0\rangle$:

$$\hat{A}|u_n\rangle=b_{n+1}|u_{n+1}\rangle+a_n|u_n\rangle+b_n|u_{n-1}\rangle \ . \tag{A1}$$

We recall that

$$|u_n\rangle=\sum_{\alpha}|\alpha\rangle u_n^{\alpha} \ , \tag{A2}$$

$$\hat{A}|\alpha\rangle=\sum_{\beta}|\beta\rangle\, \mathbf{A}^{\beta}{}_{\alpha} \ . \tag{A3}$$

Starting from an initial state $|u_0\rangle$, the construction of states $|u_n\rangle$ and coefficients (a_n,b_n) proceeds as follows.

1. Algorithm

(1) Initialize:

$$n=0 \quad (\text{current level}) \ ,$$

$$|\mathbf{u}_c\rangle=|\mathbf{u}_0\rangle \quad (\text{current vector}) \ ,$$

$$|\mathbf{u}_p\rangle=0 \quad (\text{preceding vector}) \ ,$$

$$|\mathbf{u}_f\rangle=0 \quad (\text{following vector}) \ ,$$

$$|\mathbf{u}_w\rangle=0 \quad (\text{working vector}) \ .$$

(2) Normalize $|u_c\rangle$:

$$b_n^2=\langle u_c|u_c\rangle=\sum_{\alpha,\beta}u_c^{\alpha *}\langle\alpha|\beta\rangle u_c^{\beta}=\sum_{\alpha,\beta}u_c^{\alpha *}\mathbf{S}_{\alpha\beta}u_c^{\beta} \ .$$

We define

$$|u_w\rangle=\mathbf{S}|u_c\rangle=\sum_{\alpha}|\alpha\rangle\mathbf{S}_{\alpha\beta}u_c^{\beta} \ .$$

Thus

$$u_w^{\alpha}=\sum_{\beta}\mathbf{S}_{\alpha\beta}u_c^{\beta} \ ,$$

and

$$\mathbf{u}_w=\mathbf{S}\mathbf{u}_c \ .$$

Therefore,

$$b_n^2=(\mathbf{u}_c^{\dagger},\mathbf{u}_w) \ .$$

(3) Stop if b_n^2 is too small, or if the maximal number of preassigned levels is attained.

(4) Normalize the current vector, and the working vector (if needed):

$$|u_c\rangle=|u_c\rangle/b_n, \quad \text{thus } \mathbf{u}_c=\mathbf{u}_c/b_n \ ,$$

$$|u_w\rangle=|u_w\rangle/b_n, \quad \text{thus } \mathbf{u}_w=\mathbf{u}_w/b_n \ .$$

Store $\mathbf{u}_n=\mathbf{u}_c$, if needed.

(5) Build the next vector $\hat{A}|u_c\rangle=\sum_{\beta}\hat{A}|\beta\rangle u_c^{\beta}=\sum_{\alpha,\beta}|\alpha\rangle\, \mathbf{A}^{\alpha}{}_{\beta}u_c^{\beta}$; thus

$$u_f^{\alpha}=\sum_{\beta}\mathbf{A}^{\alpha}{}_{\beta}u_c^{\beta} \ .$$

(6) Orthogonalization coefficient a_n

$$a_n=\langle u_c|\hat{A}u_c\rangle=\langle u_c|u_f\rangle=\sum_{\alpha,\beta}u_c^{\alpha *}\langle\alpha|\beta\rangle u_f^{\beta}=(\mathbf{u}_n^{\dagger},\mathbf{S}\mathbf{u}_f) \ .$$

It is not necessary to compute b_n by orthogonalization. It has still been obtained in the normalization processing of the current vector.[25]

(7) Orthogonalize $|u_f\rangle$ to preceding vectors

$$|u_f\rangle=|u_f\rangle-a_n|u_c\rangle-b_n|u_p\rangle$$

thus

$$\mathbf{u}_f=\mathbf{u}_f-a_n\mathbf{u}_c-b_n\mathbf{u}_p \ .$$

(8) Increment n, rotate the indices $p \leftarrow c \leftarrow f$, loop to step (2).

End of algorithm.

The preceding scheme shows explicitly how to build the coefficients $\mathbf{u}_n$ of the vector $|u_n\rangle$, if the mixed representation of $\hat{A}$ is known.

For the other variances, it is the same algorithm which is valid; one just takes into account the relationship between the matrices of a same operator in the various representations. The different cases, where a specified representation of $\hat{A}$ is known, are summarized in Table IV.

2. Our scheme

We recall that it is a three-step calculation.

Step 1. Use the recursion scheme for an adequate auxiliary operator, the contravariant or mixed representation of which is short ranged, in order to build an orthonormal basis set $(|u_n\rangle)$. The (a,b) coefficients are of little interest, but for controlling the linear independence of the basis.

Step 2. Project the Hamiltonian onto the basis just generated

$$\hat{H}_{\text{proj}}=\sum_{n,m}|u_n\rangle\mathbf{H}_{nm}\langle u_m| \ ,$$

with $\mathbf{H}_{nm}=\langle u_n|,\hat{H}u_m\rangle=(\mathbf{u}^{\dagger},\mathbf{H}\mathbf{u}_m)$. We recall that the overlap is the unit matrix in this representation. We thus obtain a one-dimensional chain problem, irrespective of the dimension of the initial space.

Step 3. Variant 1: diagonalize the projected Hamiltonian. Variant 2: use the ordinary recursion method to tridiagonalize $\mathbf{H}_{\text{proj}}$, with initial state $(1,0,0,\ldots)$. The coefficients (a,b) obtained in this step are those of the continued-fraction representation of $\langle u_0|\hat{G}(z)|u_0\rangle$.

TABLE IV. Computation schemes of the recursion method. $\hat{A}$ is a Hermitian operator. If $\hat{A}$ is the Hamiltonian operator, we recover the one-step recursion method. Furthermore, if $\mathbf{S}=\mathbf{I}$, all schemes turn into the traditional recursion without overlap. Only steps 5,6,5′ are specialized, according to the representation of A.

	Covariant A	Mixed A	Contravariant A
1		$\mathbf{u}_c=\mathbf{u}_0$ $\mathbf{u}_f=0$ $\mathbf{u}_p=0$ $\mathbf{u}_c=\mathbf{u}_0$ $n=0$	
2		$\mathbf{u}_w=\mathbf{S}\mathbf{u}_c$ $b_n^2=(\mathbf{u}_c^\dagger,\mathbf{u}_w)$	
3	If the maximal preassigned number of levels is attained, or b_n is close of vanishing, stop.		
4		$\mathbf{u}_c=\mathbf{u}_c b_n$ Store it if required. $\mathbf{u}_w=\mathbf{u}_w/b_n$	
5	$\mathbf{u}_f=\mathbf{A}_{\text{cov}}\mathbf{u}_c$	$\mathbf{u}_f=\mathbf{A}_{\text{mixed}}\mathbf{u}_c$	$\mathbf{u}_f=\mathbf{A}^{\text{contra}}\mathbf{u}_w$
6	$a_n=(\mathbf{u}_c^\dagger,\mathbf{u}_f)$	$a_n=(\mathbf{u}_w^\dagger,\mathbf{u}_f)$	$a_n=(\mathbf{u}_w^\dagger,\mathbf{u}_f)$
5′	$\mathbf{u}_f=\mathbf{S}^{-1}\mathbf{u}_f$		
7		$\mathbf{u}_f=\mathbf{u}_f-a_n\mathbf{u}_c-b_n\mathbf{u}_p$	
8		Rotate the indices $p\leftarrow c\leftarrow f$, increment n Loop to 2. Loop to 2.	

APPENDIX B: AN ILLUSTRATION OF THE ALGORITHMS OF APPENDIX A

A chain of five identical atoms with s orbitals

$$\mathbf{S}=\begin{bmatrix} 1 & 0.3 & 0 & 0 & 0 \\ 0.3 & 1 & 0.3 & 0 & 0 \\ 0 & 0.3 & 1 & 0.3 & 0 \\ 0 & 0 & 0.3 & 1 & 0.3 \\ 0 & 0 & 0 & 0.3 & 1 \end{bmatrix},$$

$$\mathbf{S}^{-1}=\begin{bmatrix} 1.111\,09 & -0.370\,31 & 0.122\,39 & -0.040\,64 & 0.012\,219 \\ -0.370\,31 & 1.234\,38 & -0.410\,96 & 0.135\,48 & -0.040\,64 \\ 0.122\,39 & -0.410\,96 & 1.246\,57 & -0.410\,596 & 0.122\,39 \\ -0.040\,64 & 0.135\,48 & -0.410\,596 & -0.410\,596 & -0.370\,31 \\ 0.012\,19 & -0.040\,64 & 1.234\,38 & 1.234\,28 & 1.111\,09 \end{bmatrix},$$

$$\mathbf{S}_{\text{appr}}^{-1}=\begin{bmatrix} 1 & -0.3 & 0 & 0 & 0 \\ -0.3 & 1 & -0.3 & 0 & 0 \\ 0 & -0.3 & 1 & -0.3 & 0 \\ 0 & 0 & -0.3 & 1 & -0.3 \\ 0 & 0 & 0 & -0.3 & 1 \end{bmatrix},$$

$$\mathbf{H}=\begin{bmatrix} -1 & -0.6 & 0 & 0 & 0 \\ -0.6 & -1 & -0.6 & 0 & 0 \\ 0 & -0.6 & -1 & -0.6 & 0 \\ 0 & 0 & -0.6 & -1 & -0.6 \\ 0 & 0 & 0 & -0.6 & -1 \end{bmatrix},$$

$u_0=(1,0,0,0,0)$.

TABLE V. Continued-fraction coefficients for the example of Appendix B.

Exact		Approximate	
b_{n+1}	a_n	b_{n+1}	a_n
0.333 08	−1	0.275 18	−0.836 20
0.459 01	−0.501 50	0.326 15	−0.408 42
0.365 65	−0.504 58	0.177 41	−0.294 02
0.154 86	−0.841 95	0.078 77	−0.635 13
0	−1.214 44	0	−0.990 21

TABLE VI. Energy levels and weights associated with Table V (exact). The same results are obtained by the spectral method [Eqs. (9), (42), and (43)].

Eigenvalue	Weight
−1.341 93	0.126 63
−1.230 76	0.325 00
−1	0.333 33
−0.571 42	0.175 00
−0.081 66	0.040 03

In Table V the results are reported for the continued fraction of $\langle u_0 | \hat{G}(z) | u_0 \rangle$ [Eqs. (20), and (28)–(30)] obtained by exact versions of the recursion method (Appendix A and Ballentine's biorthogonality) and with approximate $\mathbf{S}^{-1}$ ($\mathbf{S}^{-1}_{\text{approx}}$). Note that **I** has been used as matrix of the contravariant representation of the auxiliary operator in our three-step method, which also gives exact results. In Table VI we report the spectral decomposition of $g_0(z)$ corresponding to the coefficients of Table V.

---

[*] Permanent address: Laboratoire Weiss-Bauer, Université Louis Pasteur, 67000 Strasbourg, France.

[†] Permanent address: University of Calcutta, Vidyasagar College, Calcutta, India.

[1] D. W. Bullet, in *Solid State Physics,* edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1980), Vol. 35, p. 129.

[2] M. S. Daw and D. L. Smith, Phys. Rev. B **20**, 5150 (1979).

[3] R. E. Allen and J. D. Dow, Phys. Rev. B **25**, 1423 (1982).

[4] G. A. Baraff, M. Schlüter, and G. Allan, Phys. Rev. B **27**, 1010 (1983).

[5] (a) R. Riedinger and H. Dreyssé, Phys. Rev. B **27**, 2073 (1983); (b) H. Dreyssé and R. Riedinger, *ibid.* **28**, 5669 (1983); (c) R. Riedinger and H. Dreyssé, *ibid.* **31**, 3398 (1985); (d) Surf. Sci. **152/153**, 720 (1985).

[6] (a) G. Allan, Ann. Phys. (Paris) **5**, 169 (1970); (b) T. B. Grimley and C. Pisani, J. Phys. C **7**, 2831 (1974); (c) T. B. Grimley, in *Electronic Structure and Reactivity of Metal Surfaces,* edited, by E. G. Derouane and A. A. Lucas (Plenum, New York, 1976), p. 113; (d) T. L. Einstein, J. A. Herz, and J. R. Schrieffer, in *Theory of Chemisorption,* Vol. 19 of *Topics in Current Physics,* edited by J. R. Smith (Springer, Berlin, 1980), Chap. 7.

[7] A. R. Williams, P. J. Feibelmann, and N. D. Lang, Phys. Rev. B **26**, 5433 (1983).

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

[9] R. Riedinger, Phys. Lett. A **107**, 333 (1985).

[10] D. Lohez and M. Lannoo, Phys. Rev. B **27**, 5007 (1983).

[11] R. Haydock, V. Heine, and M. J. Kelly, J. Phys. C **5**, 2485 (1972).

[12] R. Haydock, V. Heine, and M. J. Kelly, J. Phys. C **8**, 2591 (1975).

[13] V. Heine, in Ref. 1, p. 1.

[14] R. Haydock, in Ref. 1, p. 216.

[15] M. J. Kelly, in Ref. 1, p. 296.

[16] R. H. Haydock, J. Phys. A **7**, 2120 (1974).

[17] R. Haydock and M. J. Kelly, J. Phys. C **8**, L290 (1975).

[18] L. E. Ballentine and M. Kolar, J. Phys. C **19**, 981 (1986).

[19] O. K. Andersen and O. Jepsen, Phys. Rev. Lett. **53**, 2571 (1984).

[20] R. H. Summerville and R. Hoffmann, J. Am. Chem. Soc. **98**, 7252 (1976).

[21] D. J. M. Fassaert and A. Van der Avoird, Surf. Sci. **55**, 291 (1976).

[22] Since the Hamiltonian operator is Hermitian, its eigenvalues are real and its diagonal spectral densities positive, even in the nonsymmetric mixed representation. $\mathbf{S}^1\mathbf{H}$ is similar to the symmetric matrix $\mathbf{S}^{-1/2}\mathbf{H}\mathbf{S}^{-1/2}$ [$=\mathbf{S}^{1/2}(\mathbf{S}^{-1}\mathbf{H})\mathbf{S}^{-1/2}$]; this property is lost for an arbitrary nonsymmetric matrix.

[23] M. J. Kelly, Surf. Sci. **43** 587 (1974).

[24] R. K. C. McLean and R. Haydock, J. Phys. C **10**, 1929 (1977).

[25] N. Gastinel, *Analyse Numérique Linéaire* (Hermann, Paris, 1966).

[26] D. G. Pettifor and N. Beer, in *Electronic Structure of Complex Systems,* Vol. 113 of *NATO Advanced Study Institute, Ser. B* (Plenum, New York, 1985).

[27] G. Allan, J. Phys. C **17**, 3945 (1983); D. M. Woodruff, S. M. Anlage, and D. L. Smith, Phys. Rev. B **36**, 1725 (1987).

[28] P. W. Anderson, Phys. Rev. Lett. **21**, 13 (1968); Phys. Rev. **181** 25 (1969).

[29] A. Kurosh, *Cours d'Algèbre Supérieure* (Mir, Moscow, 1973) (French edition).

[30] G. Gewinner, J. S. Peruchetti, R. Riedinger, and A. Jaeglé, Solid State Commun. **36**, 786 (1980).

[31] D. Aitelhabti, G. Gewinner, J. C. Peruchetti, R. Riedinger, D. Spanjaard, and G. Treglia, J. Phys. F **14**, 1717 (1984).

[32] H. Dreyssé and R. Riedinger, J. Phys. (Paris) **48**, 915 (1987).

[33] P. Turchi, F. Ducastelle, and G. Treglia, J. Phys. C **15**, 2891 (1982).

[34] D. Nguyen-Mahn, D. Mayou, D. Pavuna, F. Cyrot-Lackmann, and D. Pasturel, J. Phys. F **17**, 1309 (1987).

[35] R. Riedinger, J. Phys. F **10**, 1431 (1983).

[36] J. Chadi and M. C. Cohen, Phys. Rev. B **10**, 4988 (1974); J. L. Cunningham, *ibid.* **10**, 4988 (1974).

[37] M. Foulkes and R. Haydock, J. Phys. C **19**, 6573 (1987).