

## Electronic spectra of crystals with a subzone resummation technique

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A very accurate method is presented for the continued-fraction expansion of the electron Green's-function propagator in crystals. The novelty consists in implementing the recursion technique in decoupled subzones of the first Brillouin zone, rather than in the whole Brillouin zone or in real space. With this procedure a very large number (of the order of a hundred or more) of continued-fraction steps becomes easily accessible. Our resummation technique is applied to a number of elemental and III-V semiconductors; in particular, results for silicon, germanium, gallium arsenide, and aluminum phosphide are presented as an example. We also discuss the problem of asymptotic behavior of continued-fraction coefficients.

### I. INTRODUCTION

The continued-fraction formalism<sup>1</sup> in the study of the electronic spectra<sup>2-4</sup> of periodic solids, as well as aperiodic solids and stochastic systems, has become a valuable tool. The standard procedure<sup>1-4</sup> begins in general with a localized-orbital representation of the one-electron crystal Hamiltonian, considers a cluster as large as possible with appropriate boundary conditions, and performs recursions in real space starting from an initial state of interest. The basic difficulty when operating in real space is the relatively small size of the clusters that can be actually dealt with ( $10^4$ – $10^6$  sites or so) because of computer storage limitations; thus in most practical situations the encounter of the border of the finite cluster restricts the number of exact iterations actually accessible at no more than 10–20 steps. This is in general unsatisfactory both for a good representation of the Green's function and for the application of a suitable asymptotic truncation; in fact, experience shows that it would be in general desirable to reach at least 50–100 exact pairs of continued-fraction coefficients before some termination for the asymptotic can be safely exploited.<sup>5-10</sup>

In the case of periodic structures<sup>11-14</sup> instead of finite clusters and localized orbitals it is possible to perform the standard unitary transformations to itinerant basis functions of Bloch type. Although the number of basis functions (or degrees of freedom) in real or reciprocal space is of course unchanged, and also unchanged is the general strategy of the recursion procedure, there are several distinct advantages in performing calculations in  $\mathbf{k}$  space. The first attempt to use the recursion method in connection with a plane-wave representation of the electronic states in pseudopotential calculations is due to Brüstel *et al.*<sup>11</sup> The implementation of the recursion method in reciprocal space with delocalized functions is rather recent and opens interesting perspectives.

The first recognizable advantage has been pointed out by Anlage *et al.*;<sup>12</sup> these authors show how to exploit point-group symmetry considering an appropriate set of  $\mathbf{k}$  points in the reduced part of the Brillouin zone, thus

combining the recursion method with the special  $\mathbf{k}$  points technique.<sup>15-18</sup> Notice that exploiting the point symmetry of regular clusters is not so straightforward, although it is possible.<sup>19</sup> However the most important perspective<sup>13,14</sup> consists in *treating separately subzones of the reciprocal lattice and then resumming the partial contributions*. This last point is the key novel improvement of our method with respect to the literature. The basic idea is the full development of  $\mathbf{k}$ -space separability. One starts by dividing an arbitrary large  $\mathbf{k}$ -point cluster into a number of smaller subzones that can be tridiagonalized one by one. Once the recursion method is applied *independently* on each subzone, we obtain a set of (semi-infinite) linear chains representing them. No problem of computer memory limitation is encountered because we can choose each subzone made by a limited number of  $\mathbf{k}$  vectors. Due to the independence of the linear chains so generated, we can now process them using again the recursion method on the space made by the states by the previous recursions on the separate subzones.

Our procedure opens the road to an unprecedented number of recursion steps; it has been briefly outlined in a recent report,<sup>13</sup> where it was confined only to an ideal fictitious system known as cubium. The purpose of this paper is to show the actual implementation of the procedure in a variety of semiconductors described by a realistic Hamiltonian represented on a localized basis set. Notice that the accurate knowledge of the one-electron Green's function for the perfect crystal is of interest not only for the perfect crystals, but also in several other areas of active research,<sup>19,20</sup> including the electronic structure of impurities, heterostructures, alloys and disorder systems.

In Sec. II we consider the basic concepts and the most relevant features of our decoupling subzone resummation procedure. In Sec. III we consider several semiconductors (in particular silicon, germanium, gallium arsenide, and aluminum phosphide) described microscopically within the realistic and by now familiar  $s, p_x, p_y, p_z, s^*$  model,<sup>21</sup> and we report detailed results of Green's function and electronic spectra; the very large number of ac-

cessible iterative steps allows us to discuss also some aspects of the asymptotic behavior of continued fractions. Section IV contains the conclusions.

## II. THE $\mathbf{k}$ -SUBSPACE RECURSION PROCEDURE FOR PERIODIC STRUCTURES

In the literature the recursion method is usually implemented without exploiting explicitly the symmetry properties (if any) of the system under study; of course, in the case in which the starting seed state belongs to a given irreducible representation of the symmetry group of the Hamiltonian, all the other states of the hierarchy generated in the recursion procedure will also have the same symmetry. In the case of periodic structures, we discuss how to combine from the very beginning the recurrence concepts with the symmetry properties of the system; the resulting procedure turns out to be stable from a numerical point of view and allows us to reach an unprecedented number of recursion steps.

Consider a general periodic structure, with translation vectors  $\tau_m$  and basis vectors  $d_\mu$ . We describe microscopically<sup>22</sup> the crystal in terms of localized basis function  $\phi(\mathbf{r}-\tau_m-\mathbf{d}_\mu)$ . The translational symmetry of the system is embodied passing to the itinerant Bloch sums:

$$\Phi_{\mathbf{k}\mu}(\mathbf{r}) = \frac{1}{(N^3)^{1/2}} \sum_{\tau_m} e^{i\mathbf{k}\cdot\tau_m} \phi(\mathbf{r}-\tau_m-\mathbf{d}_\mu). \quad (1)$$

The one-electron crystal Hamiltonian  $H$  on this basis can be written in the standard form:

$$H = \sum_{\mathbf{k}} \sum_{\mu\mu'}^{BZ} |\Phi_{\mathbf{k}\mu}\rangle M_{\mu\mu'}(\mathbf{k}) \langle \Phi_{\mathbf{k}\mu'}|, \quad (2)$$

where  $\mu, \mu' = 1, \dots, n$ , with  $n$  number of independent orbitals per unit cell, and the matrix  $M_{\mu\mu'}(\mathbf{k})$  can be expressed in terms of phase factors and a (small) number of independent parameters, that can be either calculated or determined semiempirically. We can now select a state of interest  $|f_0\rangle$ , which is any desired linear combination of  $|\Phi_{\mathbf{k}\mu}\rangle$ , and we can start the recurrence relations in  $\mathbf{k}$  space, with the Hamiltonian  $H$  represented by Eq. (2). It is apparent that in this representation the Hamiltonian is block diagonal at each  $\mathbf{k}$  site, the blocks  $M_{\mu\mu'}(\mathbf{k})$  being matrices of order  $n$  equal to the number of basis orbitals centered in the atoms within the unit cell.

In general, the initial state  $|f_0\rangle$  of interest is a localized orbital of the form

$$|f_0\rangle = \sum_{\mathbf{k}}^{BZ} c_{\mathbf{k}\mu}^{(0)} |\Phi_{\mathbf{k}\mu}\rangle, \quad (3)$$

where  $c_{\mathbf{k}\mu}^{(0)} = 1/(N^3)^{1/2}$ ,  $N^3$  being the number of  $\mathbf{k}$  points in the Brillouin zone. We wish to implement the recurrence procedure with the Hamiltonian (2) and the initial state (3). Essentially we are tridiagonalizing the one-electron crystal Hamiltonian (2), whose representation in  $\mathbf{k}$  space is already factorized into small matrices. This problem can be solved with the standard recurrence concepts, the expansion coefficients  $c_{\mathbf{k}\mu}^{(n+1)}$  and the couple of parameters  $a_{n+1}, b_{n+1}$  for the  $(n+1)$ th step are given by the recurrence relations

$$\begin{aligned} c_{\mathbf{k}\mu}^{(n+1)} &= \sum_{\mu'} H_{\mu\mu'}(\mathbf{k}) c_{\mathbf{k}\mu'}^{(n)} - a_n c_{\mathbf{k}\mu}^{(n)} - b_n c_{\mathbf{k}\mu}^{(n-1)}, \\ b_{n+1}^2 &= \sum_{\mathbf{k}} \sum_{\mu}^{BZ} C_{\mathbf{k}\mu}^{(n+1)*} C_{\mathbf{k}\mu}^{(n+1)}, \\ c_{\mathbf{k}\mu}^{(n+1)} &= \frac{1}{b_{n+1}} C_{\mathbf{k}\mu}^{(n+1)}, \\ a_{n+1} &= \sum_{\mathbf{k}} \sum_{\mu\mu'}^{BZ} c_{\mathbf{k}\mu}^{(n+1)*} H_{\mu\mu'}(\mathbf{k}) c_{\mathbf{k}\mu'}^{(n+1)}, \end{aligned} \quad (4)$$

The Green's function can then be expanded in the form

$$\begin{aligned} G_{00}(E) &= \langle f_0 | 1/(E-H) | f_0 \rangle \\ &= \frac{1}{E - a_0 - \frac{b_1^2}{E - a_1 - \frac{b_2^2}{E - a_2 - \dots}}}. \end{aligned} \quad (5)$$

The basic difficulty of Eq. (4) is the simultaneous processing of the  $\mathbf{k}$  points over the whole Brillouin zone; with a standard uniform mesh,  $(2N)^3$   $\mathbf{k}$  points are required in order to evaluate  $N$  pairs of exact coefficients; the use of special points is of help but the third power law dependence still remains. Our basic novelty is to abandon this simultaneous treatment of all the Brillouin-zone points and to split them into smaller subsets that are handled separately; then the partial continued fractions so obtained are appropriately resummed and this procedure allows us to achieve hundreds (or more) exact pairs of coefficients, thus making the asymptotic region readily accessible.

Operatively we achieve our goal in the following way. Let us introduce an arbitrary division of the Brillouin zone into subzones  $S_1, \dots, S_m$  and a correspondent set of seed states  $|f_0^{(1)}\rangle, \dots, |f_0^{(m)}\rangle$ :

$$|f_0^{(i)}\rangle = \frac{1}{\sqrt{N_{S_i}}} \sum_{\mathbf{k}\mu}^{S_i} c_{\mathbf{k}\mu}^{(0)} |\Phi_{\mathbf{k}\mu}\rangle, \quad (6)$$

with  $c_{\mathbf{k}\mu}^{(0)} = 1$  if  $\mu = \nu$  and  $\mathbf{k} \in S_i$ . We can now generate a continued fraction starting from each of the  $|f_0^{(j)}\rangle$ . The set of these partial chains is nothing but a representation of the Hamiltonian (2) in the particular subspace  $S_j$ . At this point the relevant information out of the very large

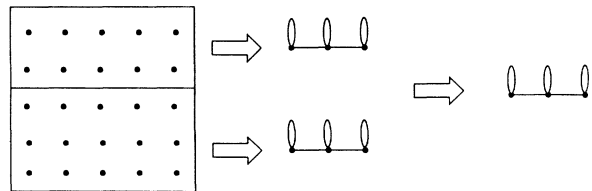


FIG. 1. Schematic representation of the resummation technique. In the left part of the figure the  $\mathbf{k}$  points of the Brillouin zone are indicated by dots. For the sake of clarity the whole Brillouin zone is partitioned only into two subzones; each of them gives rise to a continued fraction. The two partial chains are resummed into the final one.

initial number of degrees of freedom of subspace  $S$  is contained simply in the first  $N$  pairs ( $N$  of the order of 100 or so) of  $a$ 's and  $b$ 's coefficients; when the different chains are resummed the first  $N$  pairs of the final continued fraction are exact. Note also that there are no links between the chains, and so one can resum the first chain with the second, the resulting chain with the third, and so on; the only caution, of course, is the correct account of the relative "weights" of the chains (which is dictated by the square root of the degrees of freedom that they embody). The procedure of decoupling resummation in the Brillouin zone is schematically indicated in Fig. 1.

In the practical development of the calculation a technical but important point is a judicious choice of the  $\mathbf{k}$  points and of the kind of subzones. The division of the three-dimensional Brillouin zone into three-dimensional subzones has appeared of limited help; in order to obtain a significant advantage and for saving storage locations one has to consider two- or one-dimensional subzones. In the cases of IV and III-V semiconductors, discussed below, a partition of the Brillouin zone in planes does not allow more than 30–40 pairs of exact coefficients: so a division into lines of  $\mathbf{k}$  points has been necessary to reach the asymptotic region.

Note that in the spirit of resummation it is in principle possible even to consider each subzone made by a single  $\mathbf{k}$  point; however, a partition in one-dimensional zones has appeared more than sufficient in our case. A certain care must be taken also in choosing points within each subzone. The special  $\mathbf{k}$ -points technique is the optimized choice for what concerns their number, but the (computational) advantage of a uniformly weighted mesh is lost. We have thus preferred to choose a uniform mesh of  $\mathbf{k}$  points, inequivalent for inversion symmetry, so as to double the number of exact coefficients provided by a cluster of given size (we call this the "symmetrical uniform mesh"). The practical way to achieve this simplification is to shift by  $\pi/2$  the  $\mathbf{k}$  points of a standard uniform-mesh sampling the principal axes of the first Brillouin zone; the explicit form of the coordinates of the  $\mathbf{k}$  points for the symmetrical uniform mesh used in our calculation

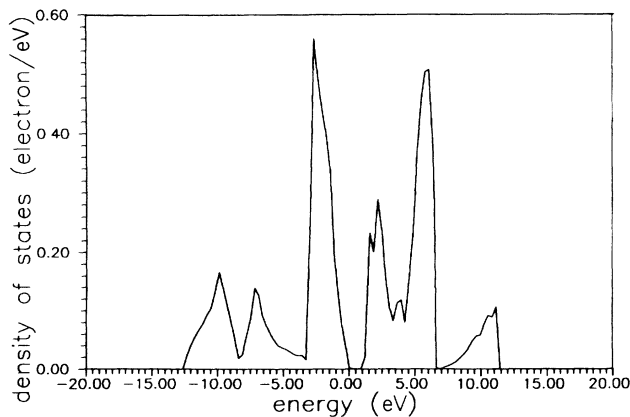


FIG. 2. Total density of states for  $s$  and  $p$  orbitals for Si evaluated with 150 exact recursion steps of the continued fraction and the two-band terminator.

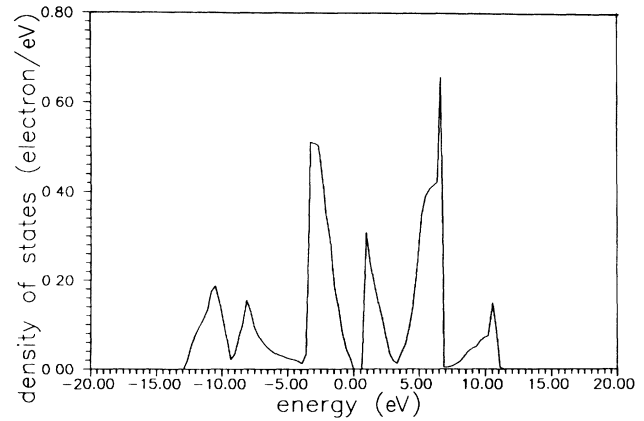


FIG. 3. Total density of states for  $s$  and  $p$  orbitals for Ge evaluated with 100 exact recursion steps of the continued fraction and the two-band terminator.

for face-centered cubic lattices is

$$\mathbf{k} = (m_1 + \frac{1}{2})(1/N)\mathbf{h}_1 + (m_2 + \frac{1}{2})(1/N)\mathbf{h}_2 + (m_3 + \frac{1}{2})(1/N)\mathbf{h}_3, \quad (7)$$

where  $0 \leq m_1, m_2, m_3 < N$ , and

$$\mathbf{h}_1 = (2\pi/a)(\bar{1}, 1, 1),$$

$$\mathbf{h}_2 = (2\pi/a)(1, \bar{1}, 1),$$

$$\mathbf{h}_3 = (2\pi/a)(1, 1, \bar{1}).$$

The number of  $\mathbf{k}$  points needed in the symmetrical uniform mesh to reach  $N$  exact recursions is  $N^3$ , for any parametrization which includes nearest-neighbor interaction only.

For what concerns partitions into subzones, we have processed  $\mathbf{k}$  points with all possible values of  $m_3$ , keeping fixed  $m_2$  and  $m_1$ ; later we have processed successively  $m_2$  and finally  $m_1$ . The time required to perform the calculation of 150 exact pairs of coefficients for a given crystal is

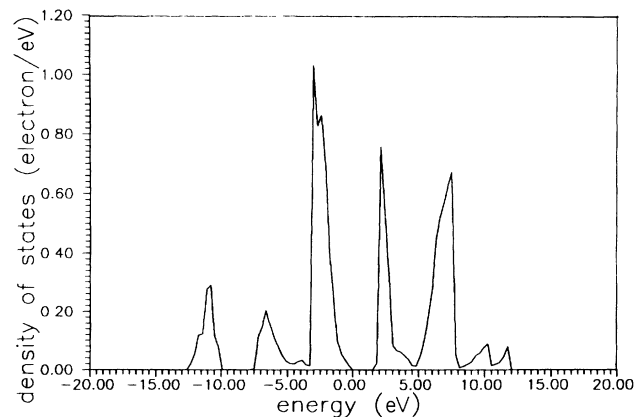


FIG. 4. Total density of states for  $s$  and  $p$  orbitals for GaAs evaluated with 100 exact recursion steps of the continued fraction and the two-band terminator.

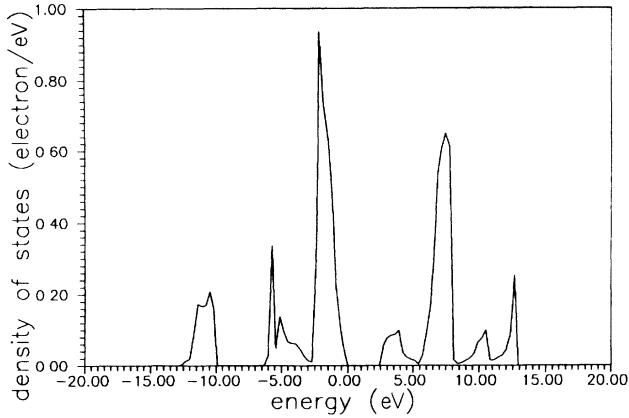


FIG. 5. Total density of states for  $s$  and  $p$  orbitals for AIP evaluated with 100 exact recursion steps of the continued fraction and the two-band terminator.

of the order of one hour CPU on the IBM 9370 computer.

### III. GREEN'S FUNCTION AND DENSITIES OF STATES FOR SEVERAL IV AND III-V SEMICONDUCTORS

In this section we report the results obtained with the described continued-fraction expansion of the Green's function. We focus basically on the projected density of

states, which is given by

$$n(E) = -\frac{1}{\pi} \lim_{\eta \rightarrow 0^+} \text{Im} \langle f_0 | 1/(E - H + i\eta) | f_0 \rangle$$

$$= -\frac{1}{\pi} \lim_{\eta \rightarrow 0^+} \text{Im} \frac{1}{E + i\eta - a_0 - \frac{b_1^2}{E + i\eta - \dots}},$$

and on the total density of states, which is obtained making the trace on the independent orbitals. Also the real part of the Green's function is of relevance for physical properties. This occurs for instance in the calculation of bound states or resonant impurity states, as well as in the calculation of the density matrix for self-consistent calculations.<sup>19</sup>

We have adopted for the tight-binding Hamiltonian the  $sp^3s^*$  parametrization of Dow *et al.*,<sup>21</sup> which has been proved very effective in many physical problems. In this model we have ten orbitals per unit cell and nearest-neighbor interaction only between orbitals. It is worthwhile to notice explicitly that this choice is not a limitation of our method, because it works also with other parametrizations regardless of the orders of neighbors included,<sup>23</sup> on the contrary, when one uses the recursion method in real space, the presence of second or higher-order interactions poses increasing difficulties and in particular the preliminary construction of the map of all interacting neighbors is essential.

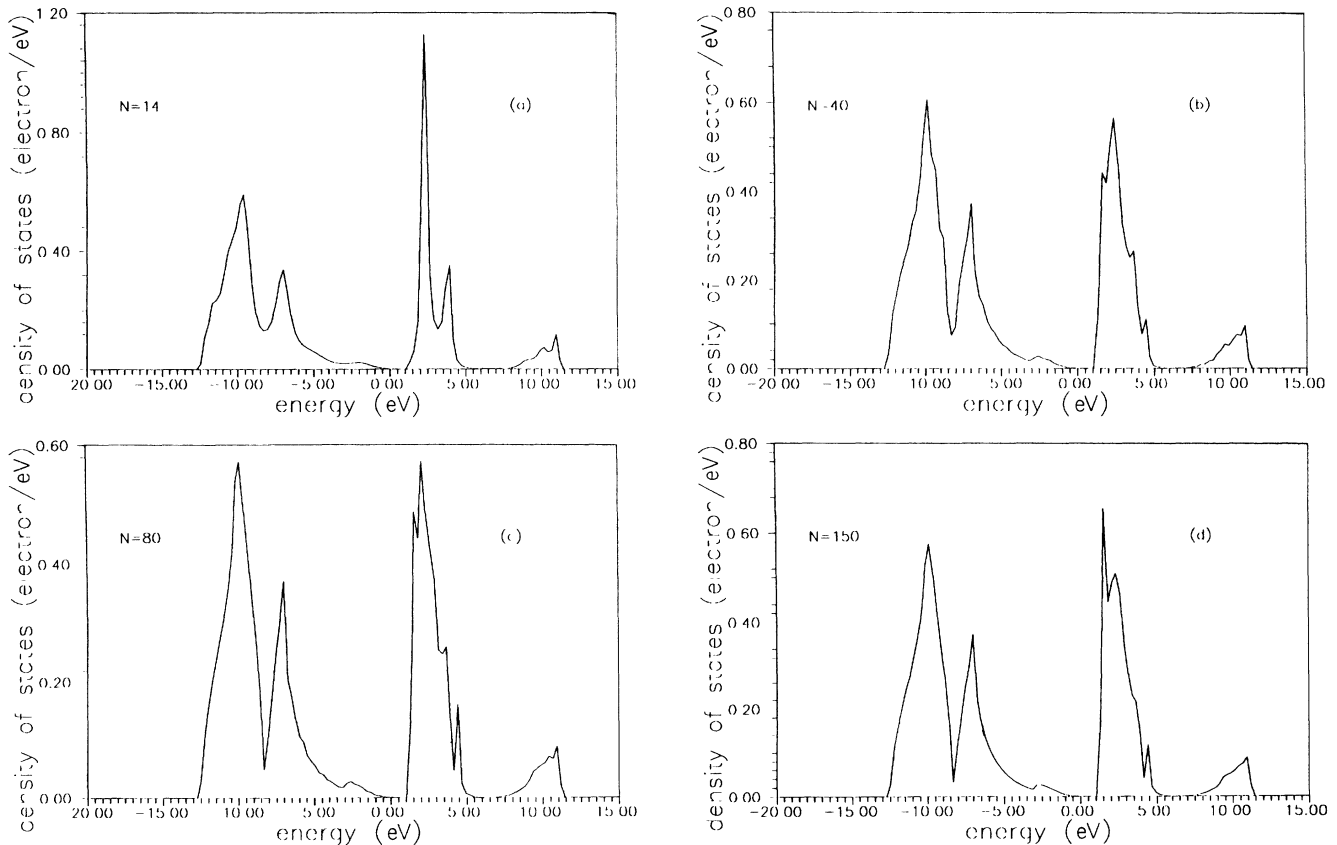


FIG. 6. Density of states for Si projected on  $s$  orbitals evaluated with 14, 40, 80, and 150 pairs of continued-fraction coefficients [(a), (b), (c), and (d), respectively], and the two-band terminator.

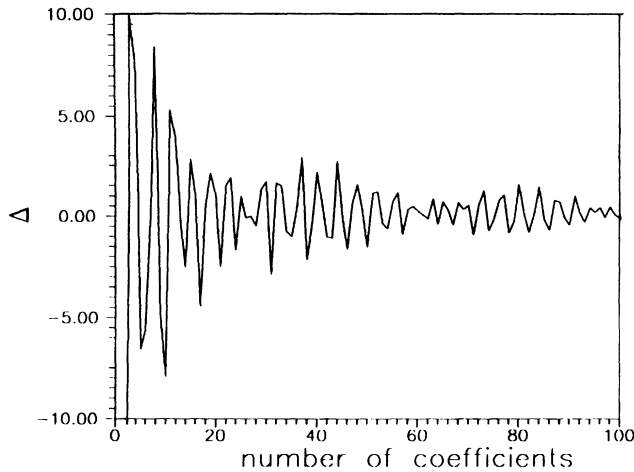


FIG. 7. Plot of the quantity  $\Delta = b_{n+1}^2 + b_n^2 + a_n^2 + A_2 + A_1 a_n$  [see Eq. (9)] versus the coefficient index  $n$  for the  $s$ -orbital projected density of states of Ge.

The  $sp^3s^*$  hybridization model, although simple, reproduces a number of relevant physical features of IV and III-V semiconductors, in particular direct and indirect gaps; however, some dispersions of the electronic states in the highest conduction bands are not correct (in particular spurious, although small, gaps in systems such as silicon or aluminum phosphide occur). We have calculated the density of states projected on single orbitals for several semiconductors. In Fig. 2, for instance, we report the total density of states for Si ( $s$  and  $p$ ) calculated with 150 pairs of coefficients. Note that a calculation of the same level, but with simultaneous processing of the whole Brillouin zone, would have required the processing of an impossible giant cluster of  $150^3$   $\mathbf{k}$  points and  $10 \times 150^3$  states. The comparison between our results and independent calculations made by means of Gilat-Raubenheimer<sup>24</sup> integration for  $s$ - and  $p$ -projected silicon densities of states shows a very good agreement. Also for the other semiconductors the electronic properties are well reproduced by our calculations. Figures 3, 4, and 5 provide the total density of states summed over  $s$  and  $p$  orbitals with 100 pairs of coefficients for Ge, GaAs, and AlP, respectively. For Figs. 2–5 the termination of the continued fraction is the “two-band model” proposed in the paper of Turchi *et al.*,<sup>9</sup> where the widths of the two bands are deduced from the corresponding values of the valence and conduction regions.

A central point in our analysis is just the achievement of the asymptotic region of the continued fractions. In fact, the problem of the representation of the Green’s function with a continued fraction can be considered solved only if one obtains a sufficiently large number of coefficients to enter the asymptotic region; in our case a mathematical and/or numerical determination of the tail is now possible in principle, although it is not certainly a trivial problem. In Fig. 6 it is clearly shown how the shape of the density of states depends on the number of coefficients used: one hundred or more exact steps are necessary to obtain a satisfactory density of states avoid-

ing spurious structures. It would be desirable to have an objective criterion to determine whether we are in the asymptotic region or not. For a nonconnected system such a criterion can be obtained from the results of the paper of Turchi *et al.*<sup>9</sup> Let us consider for simplicity a system with two disconnected allowed energy regions extending for  $E_1 < E < E_2$  and  $E_3 < E < E_4$ . Let us define the quantities

$$W = \frac{1}{2}(E_4 - E_1),$$

$$a = \frac{1}{2}(E_4 + E_1),$$

$$G = \frac{1}{2}(E_3 - E_2),$$

$$g = \frac{1}{2}(E_3 + E_2),$$

and

$$A_1 = -(g + a), \quad A_2 = ga - (W^2 + G^2)/2,$$

$$A_3 = (g - a)(W^2 - G^2)/2,$$

$$A_4 = (g - a)(aW^2 - gG^2)/2 - (W^2 - G^2)^2/8.$$

The coefficients  $a_n, b_n$ , and the band edges  $E_1, E_2, E_3$ , and  $E_4$  are connected by relations of the type

$$b_n^2 + b_{n+1}^2 + a_n^2 = -A_2 - A_1 a_n,$$

$$b_n^2 b_{n+1}^2 = (A_3 a_n - A_4)/2. \quad (8)$$

With the help of Eq. (8) we can analyze the asymptotic region. In Fig. 7 we show for Ge the quantity

$$\Delta = b_n^2 + b_{n+1}^2 + a_n^2 + A_2 + A_1 a_n \quad (9)$$

obtained from the exact coefficients evaluated versus the index  $n$ . According to (8) such a quantity should be zero in the asymptotic region, and in fact it presents damped, though irregular, oscillations as  $n$  increases.

When a large number of coefficients of the continued fraction is available a not-too-elaborate procedure of termination can also give good results. In our particular case we found that physical features of the systems in study were well preserved by the two-band terminator of Turchi *et al.*<sup>9</sup> However, there are in literature numerous efforts for alternative terminators; in particular the procedure of Luchini and Nex<sup>25</sup> proposes a linear interpolation of the coefficients between their exact and their asymptotic values. Incidentally, we verified that a phase shift between the two sets of coefficients can sensibly improve physical results, but a systematic analysis of the asymptotic behavior of the continued-fraction coefficients needs further work.

#### IV. CONCLUSIONS

In this paper we have presented a new subzone iterative procedure for obtaining the Green’s function of the one-electron crystal Hamiltonian in periodic structures. The procedure fully exploits the decoupling in  $\mathbf{k}$  space by a process of successive hierarchical ordering and elimination. It has been successfully tested for a number of semi-

conductors; to obtain comparable results in real space, one would have to handle impossibly huge clusters up to a hundred million centers. The importance of an accurate determination of the Green's function is not confined to perfect crystals, but it is of relevance also in a number of related problems, such as the electronic structure of impurities, self-consistent approaches, and homogeneous disorder. Similar techniques could also be extended to the study of layered systems, where a mixed real-

space-reciprocal-space representation is very precious. All these fields of research should benefit from the concepts and techniques presented in this paper.

#### ACKNOWLEDGMENTS

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