New procedure for evaluating a large number of continued-fraction parameters in periodic structures

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A new, very efficient procedure is provided for obtaining a large number of continued-fraction parameters for the Green's function in translationally invariant systems. This is achieved by successive applications of the recursion method to different regions in **k** space. The well-known problems connected with computer-memory limitations are thus definitively overcome.

The recursion method is usually associated[1-4] to an appropriate local basis representation of the crystal Hamiltonian on a given cluster in real space. Consider a cluster with lengths $|N_1\tau_1|$, $|N_2\tau_2|$, and $|N_3\tau_3|$ along the fundamental translation vectors; if n_c is the number of orbitals within each unit cell, the total number of degrees of freedom of the cluster is $N_t=n_cN_1N_2N_3$. It is evident that N_t soon becomes unworkable as the size of the cluster increases.

In the case of the cubium (simple cubic lattice with one s-like orbital per site) for instance, in order to obtain 50 exact pairs of parameters one should handle a cluster with about one million atoms. Thus it would be highly desirable to take advantage systematically of the symmetry operations of the underlying problem to reach as many exact steps as possible, and then to use analytic theories for extrapolating the continued-fraction parameters.[5-10] Recently important progress has been obtained with the formulation of the recursion method in the **k** space for the perfect crystals,[10] taking advantage of the point symmetry group operations via the special **k**-points techniques.[11]

The purpose of this Brief Report is to show how to handle separately groups of Bloch sums in **k** space so that we can overcome definitively any problem related with computer-storage memory limitations. As an exemplification of our procedure we discuss the **k**-space formulation of the cubium model obtaining the Green's function and the density of states to any desired accuracy. Finally, other fields that should benefit from the present procedure are briefly mentioned.

Consider the set of orthonormal localized orbitals $\{\phi_{m\mu}\}$ (centered in the positions $\mathbf{d}_\mu$ within the cell τ_m) for the representation of the crystal Hamiltonian in real space; we pass the the **k**-space representation by means of the corresponding Bloch sums

$$|\Phi_{\mathbf{k}\mu}\rangle=\frac{1}{\sqrt{N}}\sum_{\tau_m}e^{i\mathbf{k}\cdot\tau_m}|\phi_{m\mu}\rangle\ . \tag{1}$$

Within the new basis, the crystal Hamiltonian H is represented as

$$H=\sum_{\mathbf{k},\mu,\mu'}H_{\mu\mu'}(\mathbf{k})|\Phi_{\mathbf{k}\mu}\rangle\langle\Phi_{\mathbf{k}\mu'}|\ , \tag{2}$$

where the matrix elements can be determined[12,13] either theoretically or semiempirically following standard approaches.

The basic idea of our new procedure for the valuation of a large number of exact continued-fraction coefficients exploits the *separability property* of **k** space expressed by Eq. (2), i.e., the fact that application of the Hamiltonian H to a Bloch function of vector **k** does not involve excursion to other $\mathbf{k}'\neq\mathbf{k}$ points. From a large number of degrees of freedom belonging to a region in **k** space (whatever chosen, but still manageable for the computer memory) we generate an appropriate tridiagonal matrix; the first few hundred (or so) pairs of chain parameters is all we need to store out of the large number of initial degrees of freedom. The other regions in **k** space are dealt with similarly. The so-generated tridiagonal chains become then the basis of further recursions.

Let us start the iterative process with a localized state $|\phi_{0\nu}\rangle\equiv|f_0\rangle$ given by

$$|f_0\rangle=\frac{1}{\sqrt{\mathcal{N}}}\sum_{\mathbf{k}}|\Phi_{\mathbf{k}\nu}\rangle\ . \tag{3}$$

The sum over **k** runs over (a large number) $\mathcal{N}$ of appropriately chosen points in the first Brillouin zone (typically several hundred thousand special **k** points[10,11]). We divide now the set of $\mathcal{N}$ points in **k** space into an arbitrary number of subzones $S_1,S_2,\ldots,S_j$ each containing $\mathcal{N}_1,\mathcal{N}_2,\ldots$ **k** vectors, respectively ($\mathcal{N}_1+\mathcal{N}_2+\cdots+\mathcal{N}_j=\mathcal{N}$). We can rewrite Eq. (3) in the form

$$|f_0\rangle=\frac{1}{\sqrt{\mathcal{N}}}\left[(\mathcal{N}_1)^{1/2}\frac{1}{(\mathcal{N}_1)^{1/2}}\sum_{\mathbf{k}}^{S_1}|\Phi_{\mathbf{k}\nu}\rangle+\cdots+(\mathcal{N}_j)^{1/2}\frac{1}{(\mathcal{N}_j)^{1/2}}\sum_{\mathbf{k}}^{S_j}|\Phi_{\mathbf{k}\nu}\rangle\right]\ . \tag{4}$$

For every subzone S, we consider the seed state

$$|f_{0S}\rangle=\frac{1}{(\mathcal{N}_S)^{1/2}}\sum_{\mathbf{k}}^{S}|\Phi_{\mathbf{k}\nu}\rangle\equiv\sum_{\mathbf{k},\mu}^{S}c_{\mathbf{k}\mu}^{(0)}|\Phi_{\mathbf{k}\mu}\rangle \tag{5}$$

where $c_{\mathbf{k}\mu}^{(0)}=1/(\mathcal{N}_S)^{1/2}$ if $\mu=\nu$ and $\mathbf{k}\in S$, and vanishes otherwise. The standard three-term relations of the recursion method,[1] with the seed state specified by Eq. (5)

and the Hamiltonian by Eq. (2), determine the expansion coefficients $c_{\mathbf{k}\mu}^{(n)}$ $(n=1,2,\ldots)$ of the hierarchial set. The iterative expressions are as follows:

$$C_{\mathbf{k}\mu}^{(n+1)}=\sum_{\mu'}H_{\mu\mu'}(\mathbf{k})c_{\mathbf{k}\mu'}^{(n)}-a_{nS}c_{\mathbf{k}\mu}^{(n)}-b_{nS}c_{\mathbf{k}\mu}^{(n-1)}\ , \tag{6}$$

with the next terms of the hierarchy given by

$$b_{n+1,S}^2=\sum_{\mathbf{k},\mu}^{S}(C_{\mathbf{k}\mu}^{(n+1)})^*C_{\mathbf{k}\mu}^{(n+1)}\ ,$$

$$c_{\mathbf{k}\mu}^{(n+1)}=\frac{1}{b_{n+1,S}}C_{\mathbf{k}\mu}^{(n+1)}\ ,$$

$$a_{n+1,S}=\sum_{\mathbf{k},\mu,\mu'}^{S}(c_{\mathbf{k}\mu}^{(n+1)})^*H_{\mu\mu'}(\mathbf{k})c_{\mathbf{k}\mu'}^{(n+1)}\ .$$

As a result of the unitary transformation to tridiagonal form for each of the subzones, we obtain a set of independent linear chains. Let $\bar{n}$ be the actual number of interactions carried on, and $|f_{nS}\rangle$ the set of chain states generated starting from $|f_{0S}\rangle$. We can construct the operator $H_{\bar{n}}$ (including $\bar{n}+1$ states in each chain):

$$H_{\bar{n}}=\sum_S H_S\equiv\sum_S\left\{\sum_{n=0}^{\bar{n}}a_{nS}|f_{nS}\rangle\langle f_{ns}|+\sum_{n=0}^{\bar{n}-1}b_{n+1,S}(|f_{nS}\rangle\langle f_{n+1,S}|+|f_{n+1,S}\rangle\langle f_{nS}|)\right\}. \tag{7}$$

To "sum up" the obtained chains, let us consider the initial seed state of Eq. (4). Starting from it and using again the recursion procedure with the Hamiltonian expressed by Eq. (7) we can easily determine the expansion coefficients (denoted by $\gamma_{nS}^{(i)}$) of the new hierarchial set with $i=1,2,\ldots$. The iterative expressions are as follows:

$$\Gamma_{nS}^{(i+1)}=a_{nS}\gamma_{nS}^{(i)}+b_{n+1,S}\gamma_{n+1,S}^{(i)}+b_{nS}\gamma_{n-1,S}^{(i)}-a_i\gamma_{nS}^{(i)}-b_i\gamma_{nS}^{(i-1)}\ , \tag{8}$$

with the next desired coefficients given by

$$b_{i+1}^2=\sum_{n,S}(\Gamma_{nS}^{(i+1)})^*\Gamma_{nS}^{(i+1)}\ ,\quad \gamma_{nS}^{(i+1)}=\frac{1}{b_{i+1}}\Gamma_{nS}^{(i+1)}\ ,$$

$$a_{i+1}=\sum_{n,S}(\gamma_{nS}^{(i+1)})^*(a_{nS}\gamma_{nS}^{(i+1)}+b_{n+1,S}\gamma_{n+1,S}^{(i+1)}+b_{nS}\gamma_{n-1,S}^{(i+1)}).$$

It is worthwhile to point out explicitly that if the set of $\mathbf{k}$ vectors in Eq. (3) is such to assure n_{ex} exact coefficients, and $\bar{n}$ in Eq. (7) is chosen so that $\bar{n}\geq n_{ex}$, then the continued-fraction parameters provided by Eq. (8) are exact at least at the n_{ex}th step. The simplicity of the recursion relations, summarized by Eqs. (6) and (8), combined with the successive procedure of selecting out the relevant variables, are the basic reasons for the large number of continued-fraction parameters accessible with our new procedure.

As an exemplification of our procedure we have considered the case of the cubium. The Hamiltonian of Eq. (2) in the presence of one s-like Bloch sum of vector $\mathbf{k}$ becomes

$$H=\sum_{\mathbf{k}}g(\mathbf{k})|\Phi_{\mathbf{k}}\rangle\langle\Phi_{\mathbf{k}}| \tag{9}$$

with $g(\mathbf{k})=2h[\cos(k_xa)+\cos(k_ya)+\cos(k_za)]$ (the hopping integral h between two nearest-neighbor orbitals is taken as the unit of energy). The Brillouin zone of the cubium is again a simple cube, and for simplicity we sample it with a uniform mesh of $\mathbf{k}$ vectors. Among the possible ways to collect into groups the $\mathbf{k}$ vectors of the three-dimensional mesh, we have chosen to collect together the $\mathbf{k}$ vectors lying in planes perpendicular to a crystal axis (say the k_z axis). For any of these planes, we are thus left with a two-dimensional problem for which we have performed a very large number of exact recurrences. Actually in this specific case the computer-storage locations could be further reduced by separating each plane into lines of point parallel to one crystal axis (say the k_x axis), and the numerical results could also be handled with a personal computer with limited memory capabilities.

In Fig. 1(a) we plot the first 150 parameters b_n (25 coefficients were reported in the paper;[14] because of the

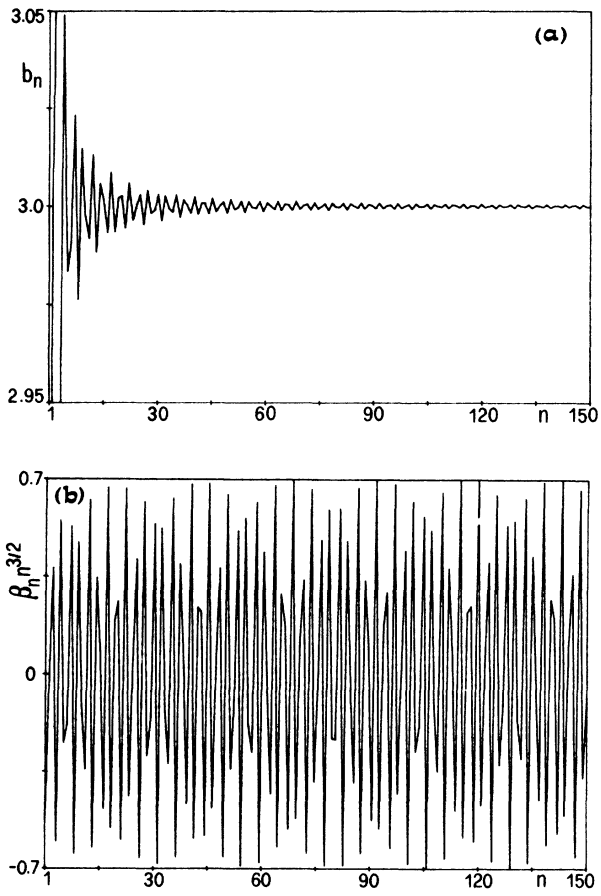

FIG. 1. (a) Recursion coefficients b_n plotted for 150 values of n. (b) Values of $\beta_n n^{3/2}\equiv(b_n-b_\infty)n^{3/2}$ plotted for 150 values of n to provide evidence of the asymptotic behavior.

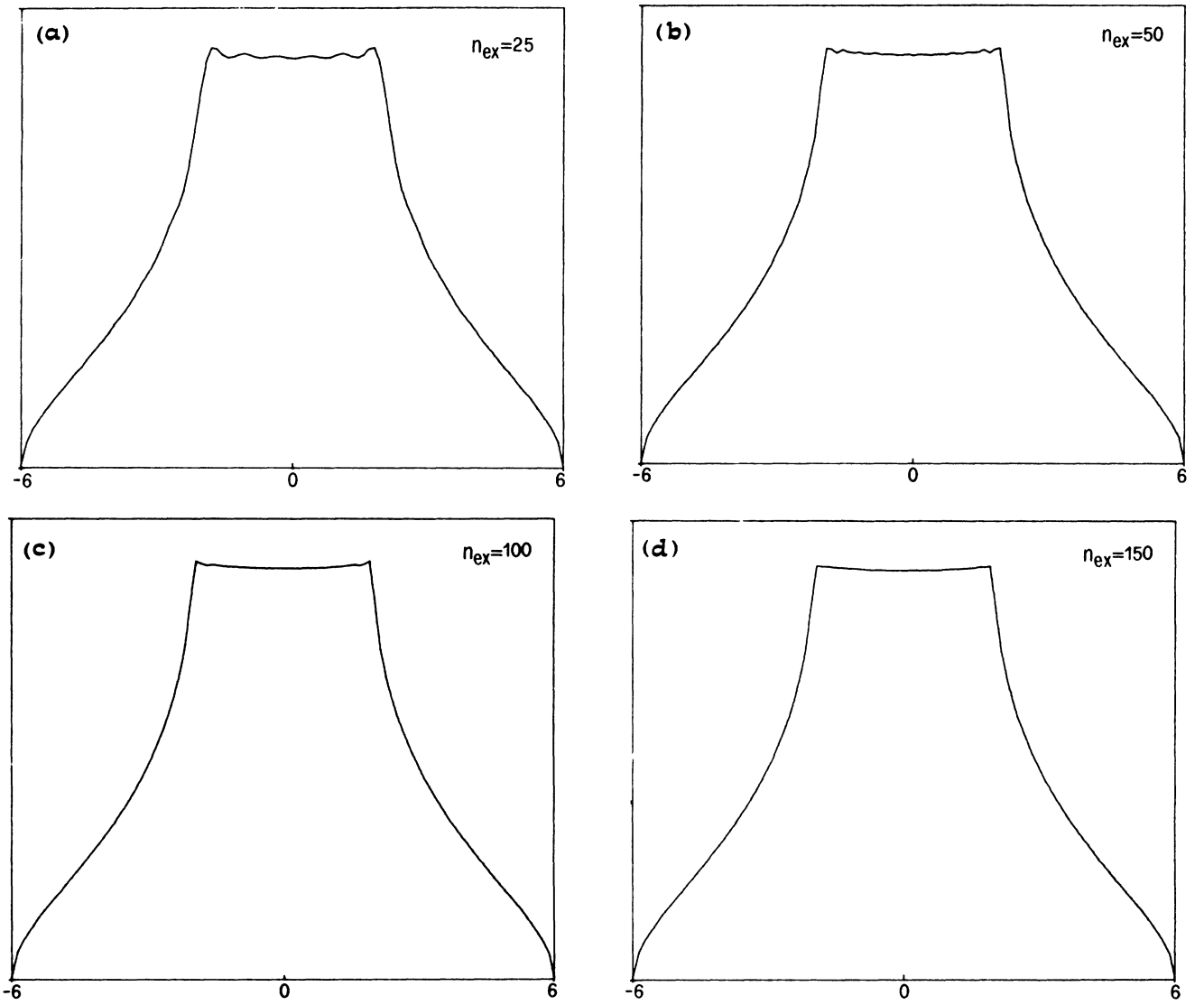

FIG. 2. Density of states of the cubium model. The exact values b_n are adopted for $n \leq n_{ex}$ [$n_{ex}=25$, 50, 100, and 150 in (a), (b), (c), and (d), respectively]; then the square-root terminator is applied.

symmetry of the problem with respect to the zero of energy, all a's equal zero). We have checked that also at higher order, our successive recursion procedure was numerically perfectly stable and reliable, with no evidence of accumulation of round-off errors. The parameters b_n correctly undergo damped oscillations around the asymptotic value $b_\infty=3$ ($h=1$), as foreseen by the theory.[5,9] It is also confirmed that because of the presence of the internal van Hove critical points in the density of states the difference $\beta_n=b_n-b_\infty$ exhibits oscillations of the type $\beta_n/n^{-3/2}\cos[(2n+1)\phi+\delta]$ [see Fig. 1(b)].

In Fig. 2 we report the density of states for the cubium; the width of the band is 12 ($h=1$). Various numbers n_{ex} of exact parameters have been used, followed by the square-root terminator

$$t(E)=\frac{1}{2b_\infty^2}[E-(E^2-4b_\infty^2)^{1/2}] .$$

It is seen that at the level reached the problem of spurious oscillations is also avoided.

In conclusion, we have here provided the road for the evaluation of a large number of continued-fraction coefficients for translationally invariant systems. The possibility of very accurate calculations of the Green's function in perfect crystals, besides being of interest in its own right, is also of value as a subsidiary tool in wide classes of problems concerning aperiodic materials. For instance, to treat the break of symmetry in perfect crystals brought about by several kinds of impurities, one often starts from the Green's function of the perfect crystal and embodies the impurity potential in an appropriate Dyson equation; the solution of these problems would greatly benefit by our procedure for calculating the Green's function in perfect crystals. Similarly, in the study of alloys in the coherent-potential approximation, again the Green's function of the perfect crystal is the basic ingredient for the subsequent account of the disorder effects.

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