

## Theory of cyclic-matrix functions with application to the analytic resolution of linear combination of atomic orbitals problems

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Cyclic-matrix functions (CMF) are shown to offer a convenient treatment of lattice periodicity, which appears to be somehow more powerful than conventional methods based on Bloch's theorem. To illustrate the ability of the method, a CMF formulation of the linear combination of atomic orbitals method, taking overlap into account, is proposed for solids of arbitrary shapes (clusters, slabs, infinite crystals, ...). Analytic expressions are obtained for the Green's-function elements, local and total density of states, thermodynamical functions, one-electron total energy, and specific heat.

### I. INTRODUCTION

The most natural mathematical embodiment of lattice periodicity is offered by cyclic-matrix functions (CMF's),<sup>1</sup> which can deal in an exact and straightforward manner with the global properties of systems perfectly periodic in space (ranging from an homoatomic cyclic molecule to a three-dimensional finite or infinite perfect crystal). Moreover, preliminary work<sup>1</sup> shows the use of the CMF yielding some exact results when the lattice is undergoing some translational symmetry loss due to the presence of a defect.

The traditional treatment of problems involving a lattice consists of reducing them, by Fourier transformation, to an eigenvalue problem, whose solution, in the form of a dispersion function, allows to express the spectral functions by numerically sampling or integrating over the reciprocal space. Because CMF theory allows nonlinear Fourier analysis, it appears to be a generalization of the conventional treatment based on Bloch's theorem; moreover, as it does not deal with individual eigenstates, it is not practically limited, as is the former theory, to perfectly periodic infinitely extended lattices. More specifically, it will be proved and illustrated in this paper that CMF theory offers at least three distinct advantages. Firstly, the theory deals directly with functions of a matrix, not merely the matrix itself. Secondly, it is applicable to functions of several cyclic matrices, not only a single one, say the Hamiltonian. Thirdly, the lattice size in the three space directions can be either small, large, or infinite; allowing a uniform treatment of lattices of various geometries: chains, strips, rods, slabs, and clusters.

The following section of this paper is devoted to a purely mathematical derivation of the CMF properties; it is self-contained without reference to crystal properties, so that other potential applications in which the lattice could be, for example, considered as an approximation to the continuum are not precluded. The derived results provide, among others, a completely unambiguous treatment of the cluster's size effect which is applied in Sec. III to linear combination of atomic orbitals (LCAO) problems,

but could as well find useful applications in the numerous schemes where clusters are used as models of extended lattices; namely, the cluster method, molecular dynamics, real-space rescaling, and moment and recursion<sup>2</sup> methods.

As an illustrative example, Sec. III proposes a CMF formulation of the LCAO method in solids. The LCAO method, a one-electron theory of solids, is based on the solution of the Schrödinger equation for a particle in a periodic field by using a set of localized orbitals; it provides a quite accurate description of the properties of a large class of solids, including covalent semiconductors and transition metals; also it constitutes a prerequisite for some more elaborate formalisms, as self-consistent schemes and density-functional theory.<sup>3</sup> One of the problems that has hampered development of the formalism in solids is the difficulty associated with the nonorthogonality of the localized orbitals; Löwdin<sup>4,5</sup> has described the problem in detail, and shows its solution to be closely linked to the evaluation of the inverse and the inverse square root of the so-called overlap matrix, but the available numerical procedures have shown to be inadequate in most cases.<sup>6</sup> More recently a renaissance of the LCAO method has taken place,<sup>7</sup> not only as an interpolation scheme (proposed by Koster and Slater<sup>8</sup>) to describe the energy bands, but also as a primary method of calculation, where the recursion techniques<sup>2</sup> play a prominent role in approaching a large class of systems; an excellent review is available<sup>9</sup> which discusses, in particular, the modern methods taking into account the overlap of the basis orbitals. The formulation in terms of CMF, rather than Bloch's waves, substantially simplifies the problem; by considering functions of a pseudo Hamiltonian which account for arbitrary hopping and overlap range, analytic expressions are derived for any element of the matrix Green's function, the local and total density of states, the one-electron energy and specific heat. That is a renewed treatment of the nonorthogonality problem in the case of perfect crystals which allows a rigorous solution.

Electronic structure of finite crystals are acknowledged to be much more complicated than that of the infinite one, nevertheless, the CMF treatment of nonsimplified

LCAO models applies fully to finite crystals, without being restricted to an  $s$ -band, first-neighbor model where the Schrödinger equation is solvable, as in previous studies.<sup>10,11</sup> Here, the difficulties associated with finite size are successfully dealt with in two different ways, the most striking result being the general statement that a physical property of a cluster can be exactly expressed in terms of this property for "translated" crystals of infinite size.

## II. GENERALIZED CYCLIC MATRICES

A cyclic matrix is the name for a square matrix whose rows (columns) can be generated from the preceding one by cyclic permutation of its elements. Consequently, the elements of an  $N \times N$  cyclic matrix can be labeled with the use of a single index  $l$ ,  $l=0,1,\dots,N-1$ , which refers to its column for an element belonging to the first row. Of particular interest are the  $N$  topological  $N \times N$  matrices<sup>12,13</sup> of order  $q$ ,  $\underline{m}_q, q=0,1,\dots,N-1$ , defined by

$$[\underline{m}_q]_l = \delta_{q,l} \text{ for } q < N. \quad (1)$$

Those matrices constitute a natural basis for the representation of the set of  $N \times N$  cyclic matrices; they are commutative and satisfy the following relations:

$$\underline{m}_0 = \underline{m}_N = \underline{I}_N, \quad (2)$$

where  $\underline{I}_N$  is the  $N \times N$  unit matrix,

$$\underline{m}_\alpha \underline{m}_\beta = \underline{m}_\beta \underline{m}_\alpha = \underline{m}_{\alpha+\beta}, \quad (3)$$

$$(\underline{m}_\alpha)^p = \underline{m}_{\alpha p}. \quad (4)$$

According to Eq. (2), we have

$$\underline{m}_\alpha = \underline{m}_\beta, \quad \alpha = \beta \pmod{N}$$

taking into account this property, we can extend the definition (1), to topological  $N \times N$  matrices of order  $q \geq N$ , that have elements in the form

$$[\underline{m}_q]_l = \begin{cases} 1, & q-l=0, N, 2N, \dots \\ 0, & q-l \neq 0, N, 2N, \dots \end{cases} \quad (5)$$

or

$$[\underline{m}_q]_l = \sum_{j=0}^{\infty} \delta_{q-l, jN}. \quad (6)$$

Two equivalent analytical expressions follow from Eqs. (5) and (6):

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$$[\underline{A}^p]_l = \sum_{\mathbf{k} \in K} \sum_{p_{\mathbf{k}}=p} (\underline{m}_{\sum p_{\mathbf{k}} k_1})_{l_1} (\underline{m}_{\sum p_{\mathbf{k}} k_2})_{l_2} (\underline{m}_{\sum p_{\mathbf{k}} k_3})_{l_3} \overline{\prod_{\mathbf{k} \in K} (\underline{a}_{\mathbf{k}})^{p_{\mathbf{k}}}}. \quad (14)$$

Now, the elements of any CMF, expressible as a power series in the variable  $\underline{A}$ , can be readily derived from the latter relation. Substitution of Eq. (7) in Eq. (14), yields

$$[\underline{m}_q]_l = N^{-1} \sum_{\tau=0}^{N-1} e^{2\pi i(q-l)\tau/N}, \quad (7)$$

$$[\underline{m}_q]_l = (2\pi)^{-1} \sum_{j=0}^{\infty} \int_{-\pi}^{\pi} e^{i(q-l-jN)\theta} d\theta, \quad (8)$$

where Eq. (7) [respectively, Eq. (8)] happens to be the most useful when  $N$  is small (respectively, large) compared to  $q-l$ . Notice that actually in Eq. (8) a single term of the sum is nonvanishing, it satisfies the relation

$$j = (q-l)/N \quad (9)$$

so that  $j \rightarrow 0$  when  $N \rightarrow \infty$ .

The limit  $N \rightarrow \infty$  of the  $N \times N$  matrix  $\underline{m}_q$  will be denoted by  $\underline{m}_q^\infty$ . Obviously,  $\underline{m}_q^\infty$  satisfies Eq. (1), so that

$$[\underline{m}_q^\infty]_l = (2\pi)^{-1} \int_{-\pi}^{\pi} e^{i(q-l)\theta} d\theta, \quad (10)$$

and an alternative form of Eq. (8),

$$[\underline{m}_q]_l = \sum_{j=0}^{\infty} [\underline{m}_q^\infty]_{l+jN}, \quad (11)$$

follows for the elements of the  $N \times N$  matrix  $\underline{m}_q$ .

Now, let us consider a simple-cubic lattice of  $N_1 \times N_2 \times N_3$  sites, with periodic boundary conditions; we are interested in generalized cyclic matrices of the form

$$\underline{A} = \sum_{\mathbf{k} \in K} \underline{m}_{k_1} \otimes \underline{m}_{k_2} \otimes \underline{m}_{k_3} \otimes \underline{a}_{\mathbf{k}}, \quad (12)$$

where  $\underline{a}_{\mathbf{k}}$  is a matrix describing some interaction existing between the sites  $0$  and  $\mathbf{k}=(k_1, k_2, k_3)$ . The summation extends over a set  $K$  of sites surrounding the origin (or any site); for a limited range of interaction, we have  $K = \{\mathbf{k} | k_i \leq K_i\}$ , otherwise  $K$  coincide with the sc lattice; by turning off some interactions, i.e., setting some  $\underline{a}_{\mathbf{k}}$ 's equal to zero, one obtains a fcc or bcc lattice.

Using the rules (2)–(4), with the caution that the matrices  $\underline{a}_{\mathbf{k}}$  may be noncommutative, different powers of the matrix  $\underline{A}$  are easily obtained in the form

$$\underline{A}^p = \sum_{\mathbf{k} \in K} \sum_{p_{\mathbf{k}}=p} \underline{m}_{\sum p_{\mathbf{k}} k_1} \otimes \underline{m}_{\sum p_{\mathbf{k}} k_2} \otimes \underline{m}_{\sum p_{\mathbf{k}} k_3} \otimes \overline{\prod_{\mathbf{k} \in K} (\underline{a}_{\mathbf{k}})^{p_{\mathbf{k}}}}, \quad (13)$$

where, by convention, the overlined factor represents the sum of products in all possible order. The elements of this generalized cyclic matrix are matrices having the same dimension as  $\underline{a}_{\mathbf{k}}$ ; they can be conveniently labeled by using the vector  $\mathbf{l}=(l_1, l_2, l_3)$ , so that

$$\begin{aligned}
[\underline{A}^p]_l &= (N_1 N_2 N_3)^{-1} \sum_{\mathbf{k}} \sum_{\tau_1=0}^{N_1-1} \sum_{\tau_2=0}^{N_2-1} \sum_{\tau_3=0}^{N_3-1} \exp \left\{ 2\pi i \left[ \left( \sum_{\mathbf{k}} p_{\mathbf{k}} k_1 - l_1 \right) \frac{\tau_1}{N_1} + \left( \sum_{\mathbf{k}} p_{\mathbf{k}} k_2 - l_2 \right) \frac{\tau_2}{N_2} \right. \right. \\
&\quad \left. \left. + \left( \sum_{\mathbf{k}} p_{\mathbf{k}} k_3 - l_3 \right) \frac{\tau_3}{N_3} \right] \right\} \prod_{\mathbf{k} \in K} (\underline{a}_{\mathbf{k}})^{p_{\mathbf{k}}} \\
&= (N_1 N_2 N_3)^{-1} \sum_{\tau_1=0}^{N_1-1} \sum_{\tau_2=0}^{N_2-1} \sum_{\tau_3=0}^{N_3-1} \exp \left[ -2\pi i \left( \frac{l_1 \tau_1}{N_1} + \frac{l_2 \tau_2}{N_2} + \frac{l_3 \tau_3}{N_3} \right) \right] \\
&\quad \times \sum_{\mathbf{k} \in K} \prod_{\mathbf{k} \in K} \left\{ \underline{a}_{\mathbf{k}} \exp \left[ 2\pi i \left( \frac{k_1 \tau_1}{N_1} + \frac{k_2 \tau_2}{N_2} + \frac{k_3 \tau_3}{N_3} \right) \right] \right\}^{p_{\mathbf{k}}} \\
&= (N_1 N_2 N_3)^{-1} \sum_{\tau_1=0}^{N_1-1} \sum_{\tau_2=0}^{N_2-1} \sum_{\tau_3=0}^{N_3-1} e^{-il \cdot \tau} [\underline{a}(\tau)]^p, \tag{15}
\end{aligned}$$

where

$$\underline{a}(\tau) = \sum_{\mathbf{k} \in K} \underline{a}_{\mathbf{k}} e^{ik \cdot \tau}, \tag{16}$$

with

$$\tau = 2\pi \left[ \frac{\tau_1}{N_1}, \frac{\tau_2}{N_2}, \frac{\tau_3}{N_3} \right], \quad 0 \leq \tau_i \leq N_i - 1 \tag{17}$$

denotes a discrete reciprocal-lattice vector. Then, the CMF elements take the following form:

$$[f(\underline{A})]_l = (N_1 N_2 N_3)^{-1} \sum_{\tau} f(\underline{a}(\tau)) e^{-il \cdot \tau}. \tag{18}$$

An alternative formulation can be obtained, following the same line of argument, by using Eq. (8) instead of Eq. (7), which is equivalent to making the transformation:

$$\begin{aligned}
N_i^{-1} \sum_{\tau_i=0}^{N_i-1} &\rightarrow (2\pi)^{-1} \sum_{j_i=0}^{\infty} \int_{-\pi}^{\pi} d\theta_i, \\
\frac{2\pi \tau_i}{N_i} &\rightarrow \theta_i, \\
l_i &\rightarrow l_i + j_i N_i,
\end{aligned} \tag{19}$$

for every space direction in Eq. (18), giving

$$[f(\underline{A})]_l = (8\pi^3)^{-1} \sum_{\mathbf{j}} \int_{-\pi}^{\pi} d\theta f(\underline{a}(\theta)) e^{-i(l+\mathbf{j}) \cdot \theta}, \tag{20}$$

where

$$\underline{a}(\theta) = \sum_{\mathbf{k} \in K} \underline{a}_{\mathbf{k}} e^{ik \cdot \theta} \tag{21}$$

and

$$\theta = (\theta_1, \theta_2, \theta_3), \tag{22}$$

$$\mathbf{j} = (j_1 N_1, j_2 N_2, j_3 N_3), \quad j_i \text{ integer}, \quad i = 1, 2, 3, \tag{23}$$

are, respectively, a continuous reciprocal-space vector and a discrete real-space vector. The simple case of an infinite

CMF corresponds obviously to  $\mathbf{j} = \mathbf{0}$  in Eq. (20) so that

$$[f(\underline{A}^\infty)]_l = (8\pi^3)^{-1} \int_{-\pi}^{\pi} d\theta f(\underline{a}(\theta)) e^{-il \cdot \theta}. \tag{24}$$

Comparison of Eqs. (20) and (24) leads to the relation

$$[f(\underline{A})]_l = \sum_{\mathbf{j}} [f(\underline{A}^\infty)]_{l+\mathbf{j}}, \tag{25}$$

which is a generalization of Eq. (11).

Although, the discrete formulation of Eq. (18) and the continuous one offered by Eqs. (20) and (25) are both valid  $\forall N_i$ ; from a practical point of view, Eq. (18) turns out to be obviously most convenient for  $N_i$  small, whereas for  $N_i$  large, Eqs. (20) and (25) should preferably be used, because the summation over  $\mathbf{j}$  which theoretically extends to infinity is in fact limited to a few terms, for the following reason. We assume that in the definition of  $\underline{A}$  in (12),  $k_i$  has the maximum value  $K_i$ ; then in  $\underline{A}^p$  the maximum topological matrix order will be  $pK_i$  which implies that  $j_i \leq (pK_i - l_i)/N_i$ , according to Eq. (9); it follows that depending on the convergence of the power-series expansion, which defines the CMF  $f(\underline{A})$ , it is possible to find a practical restricted range of summation over  $\mathbf{j}$ . Consequently, the number of infinite matrix elements needed in (25) for a fair representation of one finite matrix element is just inversely proportional to  $N_1 N_2 N_3$ , but depends quite significantly on the CMF which is being considered.

The former formulations proposed for the CMF elements are either fully discrete or fully continuous, so that they are adequate when the three  $N_i$  values are either small or large. But intermediate situations exist, where the lattice could extend widely in only one or two space directions, to which the transformation (19) in Eq. (18) should preferably be restricted, in order to obtain the appropriate formulation. An interesting example is offered by the slab: a three-dimensional lattice infinitely extended in two directions of space. A CMF defined on a *thin* slab could be written as

$$[f(\underline{A}_s)]_l = (4\pi^2 N)^{-1} \sum_{\tau=0}^{N-1} e^{-2\pi i \tau l_3 / N} \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} d\theta_1 d\theta_2 f(\underline{a}(\theta_1, \theta_2, 2\pi\tau/N)) e^{-i(l_1\theta_1 + l_2\theta_2)}, \quad (26)$$

where

$$\underline{a}(\theta_1, \theta_2, 2\pi\tau/N) = \sum_{\mathbf{k} \in K} \underline{a}_{k_1 k_2 k_3} e^{i(\theta_1 k_1 + \theta_2 k_2 + 2\pi\tau k_3 / N)}, \quad (27)$$

so that it appears as a sum of  $N$  two-dimensional CMF elements. For a *thick* slab, the following expression seems more appropriate:

$$\begin{aligned} [f(\underline{A}_s)]_l &= (8\pi^3)^{-1} \sum_{j=0}^{\infty} \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} d\theta_1 d\theta_2 d\theta_3 f(\underline{a}(\theta)) e^{-i[l_1\theta_1 + l_2\theta_2 + (l_3 + jN)\theta_3]} \\ &= \sum_{j=0}^{\infty} [f(\underline{A}^{\infty})]_{l_1, l_2, l_3 + jN}, \end{aligned} \quad (28)$$

gives the result in terms of only a few (cf. the above discussion) infinite matrix elements, which are available in analytic form from Eq. (24).

The CMF trace is another very useful quantity which is straightforward to obtain from the former relations by setting  $l=0$ ; so that the discrete formulation is

$$\text{Tr} f(\underline{A}) = \sum_{\tau} \text{Tr} f(\underline{a}(\tau)), \quad (29)$$

whereas the continuous one reads

$$\text{Tr}[f(\underline{A})] = N_1 N_2 N_3 \sum_j \text{Tr}\{[f(\underline{A}^{\infty})]_j\}. \quad (30)$$

Finally, using the transformation (19) properly, the previous results can be extended in a straightforward way to other three-dimensional lattice geometries: rods, for example, or to lower dimensions: strips and chains.

### III. CYCLIC-MATRIX FORMULATION OF THE LCAO METHOD

In the investigation of crystal electronic properties, the major role played by the LCAO method is to emphasize the part of the binding energy of the crystal originating from the broadening of atomic levels into bands. The power of the method itself is largely determined by the achievement reached in its analytic formulation. But in the traditional approach, where the electronic properties of the infinite perfect crystal result from the spectrum, few analytical results have been obtained so far, and even fewer analytical expressions of the density of states (DOS) for nondegenerate  $s$  bands;<sup>14</sup> only some approximate formulations are available.<sup>15</sup> Moreover, the nonorthogonality problem never received a full analytical treatment, and in the numerical procedures of orthonormalization, near-linear dependencies, which may appear in the set of Bloch functions used as basis functions cause problems.<sup>6</sup>

The situation appears even less satisfactory in the case of clusters; although some interesting results<sup>10,11</sup> have been obtained in closed form for some simple one atomic orbital per site models, and to say nothing of analytic solutions, the full treatment of clusters of more than  $\sim 50$  atoms, by solving the secular equation, becomes too great a computational chore.<sup>16</sup> Incidentally, for the solvable cases, the DOS was simply generated from an energy-level

diagram by centering a Gaussian of finite width at the position of each energy level.<sup>16</sup>

The model subsequently discussed, is designed to enhance physical understanding of the effect of nonorthogonality and size. So, the atoms retain their bulk position and satisfy periodic-boundary conditions, the translational symmetry is fully exploited, all possible neighbor hoppings and the most distant overlaps can be taken into account. Note that similar analysis can describe phonons and magnons.

In the LCAO method, by considering a finite set of atomic orbitals (or possibly other appropriate localized functions) of type  $\alpha$  centered on each site  $l$  of the lattice, which is denoted by the column matrix  $\underline{\phi}$ , the Schrödinger equation can be approximated by

$$[\underline{H} - E(\underline{I} + \underline{S})]\underline{\phi} = \underline{0}. \quad (31)$$

As the  $p$  normalized orbitals of type  $\alpha$  are generally not mutually orthogonal on different sites  $l$ , one defines an overlap matrix  $\underline{I} + \underline{S}$ , whose elements are the overlap integrals  $\langle \alpha, l | \beta, \mathbf{n} \rangle$ .

An interesting reformulation of Eq. (31) is as follows:

$$[(\underline{I} + \underline{S})^{-1} \underline{H} - E \underline{I}]\underline{\phi} = \underline{0}, \quad (32)$$

where we are led to define a new effective Hamiltonian:

$$\underline{H}' = (\underline{I} + \underline{S})^{-1} \underline{H}, \quad (33)$$

which is generally non-Hermitian, although it has real eigenvalues. We can now apply to this matrix the results obtained in Sec. II. If we regard the entries of the matrix  $\underline{h}_{\mathbf{k}}$  as representing hopping from one orbital  $\alpha$  in site  $0$  to another orbital  $\beta$  in site  $\mathbf{k}$ , whereas the diagonal elements of  $\underline{h}_0$  represents orbital energies and off-diagonal elements are hopping between orbitals belonging to atoms in the same site, we have

$$\underline{H} = \sum_{\mathbf{k} \in K} \underline{m}_{k_1} \otimes \underline{m}_{k_2} \otimes \underline{m}_{k_3} \otimes \underline{h}_{\mathbf{k}}. \quad (34)$$

Likewise, denoting by  $\underline{s}_{\mathbf{k}}$  the matrix whose entries are the overlap integrals between basis functions, which belongs to two sites separated by  $\mathbf{k}$ , the overlap matrix can be written as

$$\underline{S} = \sum_{\mathbf{k} \in K} \underline{m}_{k_1} \otimes \underline{m}_{k_2} \otimes \underline{m}_{k_3} \otimes \underline{s}_{\mathbf{k}}, \quad (35)$$

where the prime on the summation denotes restriction to  $\mathbf{k} \neq 0$ . The size of the  $\underline{h}_{\mathbf{k}}$  and  $\underline{s}_{\mathbf{k}}$  matrices is equal to the product of the number of atoms per primitive cell by the

number of basis functions per atom. The summations in Eqs. (34) and (35) are taken over the same set for simplicity.

From the power-series expansion of  $(\underline{I} + \underline{S})^{-1}$  and Eqs. (34) and (35), we then have

$$\begin{aligned} \underline{H}' = & \sum_{\mathbf{k}} \underline{m}_{k_1} \otimes \underline{m}_{k_2} \otimes \underline{m}_{k_3} \otimes \underline{h}_{\mathbf{k}} - \sum_{\mathbf{k}} \sum_{\mathbf{k}'} \underline{m}_{k_1+k'_1} \otimes \underline{m}_{k_2+k'_2} \otimes \underline{m}_{k_3+k'_3} \otimes \underline{s}_{\mathbf{k}} \underline{h}_{\mathbf{k}'} \\ & + \sum_{\mathbf{k}} \sum_{\mathbf{k}'} \sum_{\mathbf{k}''} \underline{m}_{k_1+k'_1+k''_1} \otimes \underline{m}_{k_2+k'_2+k''_2} \otimes \underline{m}_{k_3+k'_3+k''_3} \otimes \underline{s}_{\mathbf{k}} \underline{s}_{\mathbf{k}'} \underline{h}_{\mathbf{k}''} + \dots, \end{aligned} \quad (36)$$

where  $\underline{H}'$  appears clearly in the form of a generalized cyclic matrix. The elements of some function  $f(\underline{H}')$  can be obtained, from the results of Sec. II, through the matrix

$$\underline{h}'(\mathbf{t}) = [\underline{I} + \underline{s}(\mathbf{t})]^{-1} \underline{h}(\mathbf{t}), \quad (37)$$

where

$$\underline{h}(\mathbf{t}) = \sum_{\mathbf{k} \in K} e^{i\mathbf{k} \cdot \mathbf{t}} \underline{h}_{\mathbf{k}}, \quad (38)$$

$$\underline{s}(\mathbf{t}) = \sum_{\mathbf{k} \in K} e^{i\mathbf{k} \cdot \mathbf{t}} \underline{s}_{\mathbf{k}}, \quad (39)$$

and  $\mathbf{t}$  stands for  $\boldsymbol{\theta}$  the continuous reciprocal vector in Eq. (22), or the discrete vector  $\boldsymbol{\tau}$  in Eq. (17), or the "discrete/continuous" vector in Eq. (27).

Sometimes, one could find it more convenient<sup>17</sup> to deal with a Hermitian matrix and to transform Eq. (31) in the form

$$[(\underline{I} + \underline{S})^{-1/2} \underline{H} (\underline{I} + \underline{S})^{-1/2} - E \underline{I}] (\underline{I} + \underline{S})^{1/2} \underline{\phi} = \underline{0}. \quad (40)$$

Here, it could be desirable to find the new basis set

$$\underline{\psi} = (\underline{I} + \underline{S})^{1/2} \underline{\phi}, \quad (41)$$

that is easily achieved by calculating the elements of the CMF,  $(\underline{I} + \underline{S})^{1/2}$ , through the matrix

$$[\underline{I} + \underline{s}(\mathbf{t})]^{1/2} = \underline{I} + \frac{1}{2} \underline{s}(\mathbf{t}) - \frac{1}{8} [\underline{s}(\mathbf{t})]^2 + \frac{1}{16} [\underline{s}(\mathbf{t})]^3 - \dots \quad (42)$$

As for the effective Hamiltonian

$$\underline{H}'' = (\underline{I} + \underline{S})^{-1/2} \underline{H} (\underline{I} + \underline{S})^{-1/2}, \quad (43)$$

it is also a CMF and we need to calculate

$$\underline{h}''(\mathbf{t}) = (\underline{I} + \underline{s})^{-1/2} \underline{h} (\underline{I} + \underline{s})^{-1/2}. \quad (44)$$

That is easily achieved by developing the reciprocal of the square root of the matrix  $\underline{s}$  as

$$(\underline{I} + \underline{s})^{-1/2} = \underline{I} - \frac{1}{2} \underline{s} + \frac{3}{8} \underline{s}^2 - \frac{5}{16} \underline{s}^3 + \dots \quad (45)$$

and obtaining

$$\begin{aligned} \underline{h}''(\mathbf{t}) = & \sum_{\mathbf{k}} \underline{h}_{\mathbf{k}} e^{i\mathbf{k} \cdot \mathbf{t}} - \frac{1}{2} \sum_{\mathbf{k}} \sum_{\mathbf{k}'} (\underline{s}_{\mathbf{k}} \underline{h}_{\mathbf{k}'} + \underline{h}_{\mathbf{k}} \underline{s}_{\mathbf{k}'}) e^{i(\mathbf{k} + \mathbf{k}') \cdot \mathbf{t}} \\ & + \frac{1}{4} \sum_{\mathbf{k}} \sum_{\mathbf{k}'} \sum_{\mathbf{k}''} [\frac{3}{2} (\underline{s}_{\mathbf{k}} \underline{s}_{\mathbf{k}''} \underline{h}_{\mathbf{k}'} + \underline{s}_{\mathbf{k}'} \underline{s}_{\mathbf{k}''} \underline{h}_{\mathbf{k}} + \underline{h}_{\mathbf{k}} \underline{s}_{\mathbf{k}'} \underline{s}_{\mathbf{k}''} + \underline{h}_{\mathbf{k}'} \underline{s}_{\mathbf{k}} \underline{s}_{\mathbf{k}''}) + \underline{s}_{\mathbf{k}} \underline{h}_{\mathbf{k}'} \underline{s}_{\mathbf{k}''}] e^{i(\mathbf{k} + \mathbf{k}' + \mathbf{k}'') \cdot \mathbf{t}} - \dots \end{aligned} \quad (46)$$

Now, many functions of the effective Hamiltonians  $\underline{H}'$  or  $\underline{H}''$  can actually be obtained by introducing the matrix  $\underline{h}'(\mathbf{t})$  or  $\underline{h}''(\mathbf{t})$ , respectively, given by Eq. (37) and Eqs. (44) and (46), in the different expressions of the CMF elements which have been derived in Sec. II for the various possible crystal shapes. Therefore, at our disposal we have, respectively, Eq. (24) for infinite crystals, Eqs. (20) and (25) for large sized clusters, Eq. (18) for small clusters; completed also by Eq. (26) for thin slabs and Eq. (28) for thick slabs, and others that could be derived straightforwardly when dealing with special crystal shapes. In what follows, it will be sufficient to derive the CMF expressions for the effective Hamiltonian  $\underline{H}'$ , in the case of a crystal infinite in the three directions of space, as indeed the functions of  $\underline{H}''$  proceed readily by replacing  $\underline{h}'(\mathbf{t})$  with  $\underline{h}''(\mathbf{t})$ ; whereas a shrinkage of the crystal from an infinite to a large extension in the  $i$  direction is taken into

account by the following transformation of the CMF elements given by expression (24):

$$l_i \rightarrow l_i + j_i N_i, \quad (47)$$

$$\int_{-\pi}^{\pi} d\theta_i \rightarrow \sum_{j_i=0}^{\infty} \int_{-\pi}^{\pi} d\theta_i,$$

or if the crystal reduces itself to only a few sites in the direction  $i$ , then we use

$$\theta_i \rightarrow \frac{2\pi\tau_i}{N_i}, \quad (48)$$

$$(2\pi)^{-1} \int_{-\pi}^{\pi} d\theta_i \rightarrow N_i^{-1} \sum_{\tau_i=0}^{N_i-1}.$$

For example, to obtain the exact Green's function

$$\underline{G}(E) = [(E + i\epsilon)\underline{I} - \underline{H}']^{-1}, \quad \epsilon = 0^+ \quad (49)$$

for a Hamiltonian which is approximate, due to the finiteness of the basis set, is of much interest.<sup>18</sup> This CMF can be readily derived by using Eqs. (24) and (37), with

$$\underline{g}(E, \theta) = [(E + i\epsilon)\underline{I} - \underline{h}'(\theta)]^{-1}. \quad (50)$$

The real part is of the form

$$\begin{aligned} \text{Im } \underline{g}(E) &\simeq \epsilon \frac{\det(\underline{E}\underline{I} - \underline{h}') \frac{\partial}{\partial E} \text{adj}(\underline{E}\underline{I} - \underline{h}') - \frac{\partial}{\partial E} \det(\underline{E}\underline{I} - \underline{h}') \text{adj}(\underline{E}\underline{I} - \underline{h}')}{[\det(\underline{E}\underline{I} - \underline{h}')]^2 + \epsilon^2 \left[ \frac{\partial}{\partial E} \det(\underline{E}\underline{I} - \underline{h}') \right]^2} \\ &= -\pi \frac{\text{adj}(\underline{E}\underline{I} - \underline{h}')}{\frac{\partial}{\partial E} \det(\underline{E}\underline{I} - \underline{h}')} \delta \left[ \frac{\det(\underline{E}\underline{I} - \underline{h}')}{\frac{\partial}{\partial E} \det(\underline{E}\underline{I} - \underline{h}')} \right], \end{aligned} \quad (53)$$

where we have used the representation

$$\delta(x) = \frac{1}{\pi} \frac{\epsilon}{\epsilon^2 + x^2}$$

and the property

$$f(x)\delta(f(x)) = 0$$

of the Dirac  $\delta$  function. Another property

$$\delta(f_1 f_2) = f_2^{-1} \delta(f_1)$$

is used now to rewrite Eq. (53) in the form

$$\text{Im } \underline{g}(E) = -\pi \text{adj}(\underline{E}\underline{I} - \underline{h}') \delta(\det(\underline{E}\underline{I} - \underline{h}')). \quad (54)$$

Making use of the relation<sup>19</sup>

$$\frac{\partial}{\partial E} \det[\underline{A}(E)] = \text{Tr} \left[ \text{adj}[\underline{A}(E)] \frac{\partial}{\partial E} \underline{A}(E) \right]$$

and

$$\delta(f(E)) = \sum_n \frac{\delta(E - E_n)}{|f'(E_n)|},$$

we then have

$$\text{Im } \underline{g}(E) = -\pi \sum_n \frac{\text{adj}(\underline{E}\underline{I} - \underline{h}')}{\text{Tr}[\text{adj}(\underline{E}\underline{I} - \underline{h}')] } \delta(E - E_n), \quad (55)$$

where  $E_n$  is an eigenvalue of  $\underline{h}'$ , that is a solution of the secular equation

$$\det(\underline{E}\underline{I} - \underline{h}') = 0.$$

The local density of states<sup>20</sup> at an orbital consists of one diagonal element of the matrix (49):

$$n_\alpha(E) = -\pi^{-1} [\text{Im } \underline{G}(E)]_{0,\alpha\alpha}, \quad (56)$$

which can be rewritten on account of Eq. (55) as

$$[\text{Re } \underline{G}(E)]_I = (2\pi)^{-3} \int_{-\pi}^{\pi} [\underline{E}\underline{I} - \underline{h}'(\theta)]^{-1} e^{-iI \cdot \theta} d\theta. \quad (51)$$

Turning now to the imaginary part, we write

$$\underline{g}(E) \simeq \frac{\text{adj}(\underline{E}\underline{I} - \underline{h}') + i\epsilon \frac{\partial}{\partial E} \text{adj}(\underline{E}\underline{I} - \underline{h}')}{\det(\underline{E}\underline{I} - \underline{h}') + i\epsilon \frac{\partial}{\partial E} \det(\underline{E}\underline{I} - \underline{h}')}, \quad (52)$$

where  $\text{adj}(\underline{A})$  denotes the adjoint of the matrix  $\underline{A}$ ; also

$$n_\alpha(E) = (2\pi)^{-3} \sum_n \int_{-\pi}^{\pi} \frac{[\text{adj}(\underline{E}\underline{I} - \underline{h}')]_{\alpha\alpha}}{\text{Tr}[\text{adj}(\underline{E}\underline{I} - \underline{h}')] } \delta(E - E_n) d\theta. \quad (57)$$

A summation over the diagonal elements also yields the total electronic DOS in the form

$$n(E) = (2\pi)^{-3} \sum_n \int_{-\pi}^{\pi} \delta(E - E_n(\theta)) d\theta. \quad (58)$$

However, a main interest of the CMF scheme is to allow direct calculations of a range of properties without appealing to the DOS for evaluating integrals over the Brillouin zone; this causes a great simplification and allows a direct comparison with experimental data, avoiding intermediate calculations. This point will now be illustrated by derivations of the one-electron energy and specific heat. The one-electron energy is formally defined by integration over the occupied part of the spectrum as

$$U = \sum_n E_n f(E_n) = \int_{-\infty}^{\infty} E n(E) f(E) dE, \quad (59)$$

where  $f$  is the Fermi-occupation factor

$$f(E) = \{1 + \exp[\beta(E - \mu)]\}^{-1}, \quad (60)$$

$\mu$  being the chemical potential and  $\beta = (k_B T)^{-1}$  the reciprocal temperature. In matrix notation, Eq. (59) can be rewritten in the form

$$U = \text{Tr}[\underline{H}' f(\underline{H}')] , \quad (61)$$

which yields the one-electron energy per site

$$u = (2\pi)^{-3} \int_{-\pi}^{\pi} \text{Tr}(\underline{h}' \{ \underline{I} + \exp[\beta(\underline{h}' - \mu \underline{I})] \}^{-1}) d\theta, \quad (62)$$

and by differentiating we obtain the electronic specific heat at low temperature:

$$C_v/k_B = \beta^2 (2\pi)^{-3} \int_{-\pi}^{\pi} \text{Tr}((\underline{h}' - \mu \underline{I}) \{ \underline{I} + \exp[\beta(\underline{h}' - \mu \underline{I})] \}^{-2} \exp[\beta(\underline{h}' - \mu \underline{I})]) d\theta. \quad (63)$$

The free energy and other thermodynamical functions are attainable in the same manner.

Remember that the above results can be readily extended to crystals of other shapes by using transformations (47) and (48). As an illustrative example of the interesting results to be expected in such cases, we consider the DOS for the  $s$  band of a thin slab ( $N \geq 2$ ) and assume isotropic, first-neighbor interactions. For an orthogonal basis, with a proper choice of the energy's origin, Eq. (27) can be written as

$$\underline{h}(t) = 2E_1 [\cos\theta_1 + \cos\theta_2 + \cos(2\pi\tau/N)], \quad (64)$$

and from Eqs. (26) and (58), the DOS per site of the slab is

$$n_s(E) = (4\pi^2 N)^{-1} \sum_{\tau=0}^{N-1} \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \delta(E - 2E_1 \cos(2\pi\tau/N) - 2E_1(\cos\theta_1 + \cos\theta_2)) d\theta_1 d\theta_2. \quad (65)$$

On the other hand, the DOS of an infinite square lattice is

$$n_2(E) = (4\pi^2)^{-1} \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \delta(E - 2E_1(\cos\theta_1 + \cos\theta_2)) d\theta_1 d\theta_2, \quad (66)$$

hence, Eq. (65) can be rewritten as

$$n_s(E) = N^{-1} \sum_{\tau=0}^{N-1} n_2[E - 2E_1 \cos(2\pi\tau/N)], \quad (67)$$

which is a self-explanatory result.

Finally, from those examples, the CMF method has proven its ability to treat rigorously the influence of size

and geometry on the electronic properties of finite crystals. In the case of semi-infinite crystals, the CMF's have also been useful to derive exact DOS,<sup>1</sup> whereas other analytical expressions will be reported in the near future. Subsequently, we plan to extend those result to the most realistic case of finite-size crystals with nonperiodic boundary conditions.

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