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1. Introduction.

Formulating the physical properties of a crystal perturbed by the presence of a defect is a challenge, regarding the necessity to meet two conflicting requirements: to fully exploit the translational symmetry of the host crystal and to describe properly the defect itself. In this respect, many methods which have been introduced and used are not fully satisfactory, for example: the cluster and defect-molecule calculations fail to give band-edges relative to which the bond-state energy (if any) can be referred [1]; supercell calculations introduce some spurious effects [2]; numerical calculations from the method of moments [3] appear to be somewhat unstable; ...The Green's function formulation suffers from none of these drawbacks. This function can be formally obtained via a perturbation expansion of the Dyson equation whose complexity increases with the size of the perturbed space and the dimensionality of the crystal, so that heretofore closed analytical expressions for the Green function matrix elements have been obtained in the cases where the perturbation is diagonal only, i.e. vibrations of a linear chain containing a single substitutional isotopic impurity [4] or the related problem of a diagonal perturbation in a one-dimensional TBM (tight-binding model) [3]; or when the perturbation is off-diagonal only, i.e. an ideal surface in a (simple cubic) SC crystal [6]. Therefore the direct and natural description of the imperfect crystal in real space which is offered by an infinite matrix representation of the Hamiltonian seems attractive; especially if it can directly yield analytical closed expressions for the crystal properties, not limited to the Green function, without appealing to Bloch's theorem, Elucidation of FIGCM (functions of infinite generalized cyclic matrix) properties [7, 8] allowed recently to achieve this goal, in the case of perfect crystals; generalization of the method to imperfect crystals is initiated in the present paper, by considering two simple models, namely the nearest-neighbor's band TBM of a linear chain with a vacancy and the SC lattice with a surface, in order to prove its feasibility. In both considered cases, any function of the Hamiltonian could be obtained in infinite matrix form, from which were directly derived exact analytical expressions; so hereafter are given such expressions for the diagonal and off-diagonal elements of the Green function, for the local and total density of states, for the free-energy.

Those results are illuminating with regard to the basic properties of the crystal vacancy and surface. Moreover, the method appears to make simple models of imperfect crystals so easily accessible to exact analysis, that it can be reasonably expected to be powerful in dealing with more realistic defect problems, such as multiband, self-consistent... calculations.
2. Some useful matrix properties.

The one-particle Hamiltonian of a perfect cubic crystal can be represented in terms of cyclic matrices $m_p$. By introducing some sparse diagonal matrices $D_p$ to account for the presence of the defects, the representation of imperfect crystals is readily obtained. Therefore, we first discuss some useful properties of classes of matrices $m_p$ and $D_p$ and their commutation relations too.

Let $m_p$ be the $N \times N$ topological cyclic matrix of order $p$, whose elements are given by

$$[m_p]_{az} = \delta_{az} \quad (a = 0, 1, \ldots, N - 1) \quad (1)$$

for $p \geq 0$, other rows being obtained by cyclic permutation; and $m_p$ is the transpose and inverse of $m_p$. They satisfy the following identities

$$m_0 = m_N = I_N \quad (2)$$
$$m_p m_q = m_{p+q} \quad (3)$$
$$(m_p)^n = m_{p+n} \quad (4)$$

Another identity which proved to be very useful in dealing with perfect periodic crystals [8] is

$$C_p(m_1) = m_p \quad (5)$$

where

$$M_p = m_p + m_{-p} \quad (6)$$

is the symmetric topological cyclic matrix of order $p$ and $C_p(x)$ is the $p$th order Chebyshev polynomial of the second kind [9], obeying the recurrence formulae

$$C_{p+1}(x) = 2x C_p(x) - C_{p-1}(x) \quad (p \geq 1) \quad (7)$$
$$C_{p+2}(x) = 2x C_p(x) - C_{p-2}(x) \quad (p \geq 2) \quad (8)$$

Note that the relation (5) is valid for $p < N$ only, because from equations (2) and (4), we have

$$m_1^N = I_N \quad (9)$$

When a $N \times N$ matrix $A$ is expected to retain something of the property expressed by (5); it is convenient to consider an expansion in the set of orthogonal Chebyshev polynomials in the form

$$A^p = \sum_{q=0}^{N-1} \langle x^q, C_p(x) \rangle C_q(A) \quad (p < N) \quad (10)$$

where the inner product is

$$\langle f(x), C_q(x) \rangle = (2 \pi(1 + \delta_q))^{-1} \int_{-1}^{1} (1 - x^2)^{-1/2} f(2x) C_q(2x) \, dx \quad (11a)$$
$$= (\pi(1 + \delta_q))^{-1} \int_{0}^{\pi} f(2 \cos \theta) \cos q \theta \, d\theta \quad (11b)$$

making use of the relation $C_q(2 \cos \theta) = 2 \cos q \theta$; the terms $q > p$ in equation (10) cancel out, just as all terms with $q$ and $p$ having different parities. Now considering a function of $A$ expressible as an infinite power series expansion, we have from (10)

$$f(A) = \lim_{N \rightarrow \infty} \sum_{q=0}^{N-1} \langle f(x), C_q(x) \rangle C_q(A) \quad (12)$$

Generalization to three dimensions is readily obtained by means of the following relations

$$A_1^p \otimes A_2^q \otimes A_3^r = \sum_{q_1+q_2+q_3=0}^{N-1} \langle x_1^{q_1} x_2^{q_2} x_3^{q_3}, C_{q_1}(x_1) C_{q_2}(x_2) C_{q_3}(x_3) \rangle C_{q_1}(A_1) \otimes C_{q_2}(A_2) \otimes C_{q_3}(A_3) \quad (13)$$

$$f(A_1 \otimes A_2 \otimes A_3) = \lim_{N \rightarrow \infty} \sum_{q_1+q_2+q_3=0}^{N-1} \langle f(x_1, x_2, x_3), C_{q_1}(x_1) C_{q_2}(x_2) C_{q_3}(x_3) \rangle C_{q_1}(A_1) \otimes C_{q_2}(A_2) \otimes C_{q_3}(A_3) \quad (14)$$

with the inner product

$$\langle f(x_1, x_2, x_3), C_{q_1}(x_1) C_{q_2}(x_2) C_{q_3}(x_3) \rangle = \left[ (2 \pi)^3 (1 + \delta_{q_1}) (1 + \delta_{q_2}) (1 + \delta_{q_3}) \right]^{-1}$$
$$\times \int_{-1}^{1} \int_{-1}^{1} \int_{-1}^{1} d\epsilon_1 \, d\epsilon_2 \, d\epsilon_3 \left[ (1 - x_1^2) (1 - x_2^2) (1 - x_3^2) \right]^{-1/2} f(2 x_1, 2 x_2, 2 x_3)$$
$$\times C_{q_1}(2 x_1) C_{q_2}(2 x_2) C_{q_3}(2 x_3) = \left[ (2 \pi)^3 (1 + \delta_{q_1}) (1 + \delta_{q_2}) (1 + \delta_{q_3}) \right]^{-1}$$
$$\times \int_{0}^{\pi} \int_{0}^{\pi} \int_{0}^{\pi} d\theta_1 \, d\theta_2 \, d\theta_3 f(2 \cos \theta_1, 2 \cos \theta_2, 2 \cos \theta_3) C_{q_1}(\cos \theta_1) C_{q_2}(\cos \theta_2) C_{q_3}(\cos \theta_3) \quad (15)$$
Other useful identities are derived from
\[ C_q(2 \cos \theta) = 2 \cos q\theta \]
as
\[ 2^{p-1} = \sum_{q=0}^{N-1} \langle x^p, C_q(x) \rangle, \quad (16) \]
and
\[ f(2) + f(-2) = 4 \sum_{q=0}^{(N-1)/2} \langle f(x), C_2q(x) \rangle. \quad (17) \]

Turning now to the diagonal \( N \times N \) matrices defined by
\[ [D_p]_{ab} = \delta_{a,b} \delta_{a,p}, \quad (p \geq 0) \]
\[ [D_{-p}]_{ab} = [D_{N-p}]_{ab} = \delta_{a,b} \delta_{a,-p}, \quad (p \geq 0) \quad (19) \]
they clearly satisfy the following identities
\[ D_p^2 = D_p, \quad (20) \]
\[ D_p D_q = 0 \quad (p \neq q). \quad (21) \]

Finally, the matrices \( m_p \) and \( D_p \) do not commute, but rather obey the rule
\[ D_p m_q = m_q D_{p+q} \text{ or } m_q D_p = D_{p-q} m_q. \quad (22) \]


Let us consider a one-dimensional chain of \( N \) sites, with periodic boundary conditions and nearest neighbours interactions only. A vacancy is located at the origin, so that the Hamiltonian of the system is
\[ H_v = \varepsilon(I - D_0) + \beta(I - D_0 - D_{-1}) m_1 + \]
\[ + m_{-1}(I - D_0 - D_{-1}), \quad (23) \]
where \( \varepsilon \) is the atomic energy at the occupied sites and \( \beta \) the transfer energy. Changing the zero and scale of energy, it is convenient to use the reduced Hamiltonian
\[ H = \beta^{-1}(H_v - \varepsilon I) \quad (24a) \]
\[ = \alpha D_0 + (I - D_0 - D_{-1}) m_1 + m_{-1}(I - D_0 - D_{-1}), \quad (24b) \]
where \( \alpha = -\varepsilon/\beta \).

We now proceed to derive an expression of an arbitrary matrix function \( f(H) \) in the form of equation (12). The \( C_q(H) \) matrices exhibit different forms according to the parity of \( p \). Clearly we have first
\[ C_q(H) = 2 I; \quad (25) \]
and making use of equations (2-4; 7, 8; 18-22), we find the recurrence relations

\[ C_{2p}(H) = C_{2p}(x) D_0 - D_p - D_{-p} - (D_{p-1} + D_{-p-1}) m_2 - m_{-2}(D_{p-1} + D_{-p-1}) - \cdots + + \left( I - \sum_{k=0}^{2p} D_{-k} \right) m_{2p} + \sum_{k=0}^{2p} D_{-k} \right) \]
\[ C_{2p+1}(H) = C_{2p+1}(x) D_0 - (D_p + D_{-p}) m_1 - m_{-1}(D_p + D_{-p}) - (D_{p-1} + D_{-p-1}) m_3 - - m_{-3}(D_{p-1} + D_{-p-2}) - \cdots + \left( I - \sum_{k=0}^{2p+1} D_{-k} \right) m_{2p+1} + m_{-2p+1} \left( I - \sum_{k=0}^{2p+1} D_{-k} \right); \quad (27) \]
whose first terms are proved to be correct in appendix A. Now substitution of equations (25, 26, 27) into equation (12) yields, for \( N \to \infty \) as understood subsequently,
\[ f(H) = \langle f(x), C_0(x) \rangle \left( 2 I + \sum_{q=1}^{N-1} \langle f(x), C_q(x) \rangle C_q(x) D_0 - \sum_{q=2}^{N-1} \langle f(x), C_q(x) \rangle (D_{q/2} + D_{-q/2}) + + \langle f(x), C_1(x) \rangle m_1 - \sum_{q=2}^{N-1} \langle f(x), C_q(x) \rangle \left( D_{q-2} + D_{-q-2} \right) m_1 - \cdots + = 2 \langle f(x), C_0(x) \rangle (I - D_0) + f(x) D_0 - \sum_{l=1}^{(N-1)/2} \langle f(x), C_{2l}(x) \rangle (D_l + D_{-l}) + \langle f(x), C_1(x) \rangle m_1 - \sum_{l=0}^{N/2-1} \langle f(x), C_{2l+1}(x) \rangle (D_l + D_{-l-1}) m_1 - \cdots. \quad (28) \]
We note that the first term in equation (28) is just the contribution of the chain without defect, that should be obtained upon setting \( D_0 = D_{-1} = 0 \) in equation (24b); whereas the following terms represent the contribution of the vacancy to \( f(H) \).
The matrix Green's function $G(z) = (zI - H)^{-1}$ is readily obtained from equation (28) in the form

$$G(z) = 2 \left\langle (z - x)^{-1}, C_0(x) \right\rangle (I - D_0) + \left( z^{-1} \right) D_0 - \sum_{i=1}^{(N-1)/2} \left\langle (z - x)^{-1}, C_{2i}(x) \right\rangle (D_i + D_{-i}) + \left\langle (z - x)^{-1}, C_4(x) \right\rangle m_1 - \sum_{i=0}^{N/2-1} \left\langle (z - x)^{-1}, C_{2i+1}(x) \right\rangle (D_i + D_{-i-1}) m_1 - ..., \quad (29)$$

yielding the following expressions for the diagonal elements

$$G_{0,0}(z) = (z - x)^{-1},$$

$$G_{l,l}(z) = G_{N-l,N-l}(z) = 2 \left\langle (z - x)^{-1}, C_0(x) \right\rangle - \left\langle (z - x)^{-1}, C_2(x) \right\rangle$$

$$= \left\langle (z - x)^{-1}, 2 C_0(x) - C_2(x) \right\rangle$$

$$= \frac{2}{\pi} \int_0^\pi \frac{\sin^2 2\theta d\theta}{z - 2 \cos \theta} \quad (l \neq 0) \quad (31)$$

and for the first off-diagonal elements

$$G_{l,l+1} = \left\langle (z - x)^{-1}, C_1(x) - C_{2l+1}(x) \right\rangle$$

$$= \frac{1}{\pi} \int_0^\pi \frac{\cos \theta - \cos (2l + 1) \theta d\theta}{z - 2 \cos \theta} \quad (32)$$

The local density of states is defined by

$$n_l(E) = - \pi^{-1} \text{Im} \ G_l(E + \theta); \quad (33)$$

taking into account the relation

$$\text{Im} \ (E + \theta + x)^{-1} = - \pi \delta(E + x), \quad (34)$$

we have from equations (30) and (31)

$$n_0(E) = \delta(E - x),$$

$$n_l(E) = n_{N-l}(E) = 2 \left\langle \delta(E - x), C_0(x) \right\rangle - \left\langle \delta(E - x), C_2(x) \right\rangle.$$  

$$= \frac{1 - C_2(E)/2}{\pi(1 - E^2/4)^{1/2}} \quad (l \neq 0). \quad (37)$$

The total density of states is obtained by summing over $l$ expressions (35) and (36) as

$$n(E) = \delta(E - x) + 2(N - 1) \left\langle \delta(E - x), C_0(x) \right\rangle - 2 \sum_{i=1}^{(N-1)/2} \left\langle \delta(E - x), C_{2i}(x) \right\rangle,$$

$$= \delta(E - x) + 2N \left\langle \delta(E - x), C_0(x) \right\rangle - 2 \sum_{i=0}^{(N-1)/2} \left\langle \delta(E - x), C_{2i}(x) \right\rangle.$$  

Making use of equation (17), simplification occurs in the form

$$n(E) = \delta(E - x) + 2N \left\langle \delta(E - x), C_0(x) \right\rangle - \frac{4}{3}[\delta(E - 2) + \delta(E + 2)],$$

$$= N\pi^{-1}(1 - E^2/4)^{-1/2} + \delta(E - x) - \frac{4}{3}[\delta(E - 2) + \delta(E + 2)]. \quad (40)$$

Analysing this explicit expression of the spectrum, we note that the density of states of the perfect chain is recovered in the first term, whereas the second term represents a localized bound state at zero energy (remembering the change of variables in equation (24b)), which lies outside the band, for any realistic assumption concerning the $\epsilon$ and $\beta$ parameters; the two negative $\delta$ functions in the third term are found to be exactly situated at the band edges, so that they tend to smooth out these Van Hove singularities. Finally, when integrated, equation (40) contains $N$ electrons, as required.

Many thermodynamic functions may be written as the trace of some matrix function, which from equation (28), has the form

$$\text{Tr} \ f(H) = 2(N - 1) \left\langle f(x), C_0(x) \right\rangle + f(x) - \sum_{i=1}^{(N-1)/2} \left\langle f(x), C_{2i}(x) \right\rangle,$$  

$$= \pi(1 - E^2/4)^{1/2} \quad (41)$$
and taking into account equation (17)

\[ \text{Tr } f(H) = 2N \left< f(x), C_0(x) \right> + f(\mu) - \frac{1}{2} [f(2) + f(-2)]. \]  \hspace{1cm} (42)

Bypassing expression of the spectrum, the latter equation yields directly, for example, the free energy with respect to the chemical potential \( \mu \), which may be written from the spectral theorem as

\[ F = -kT \text{Tr } \log \left[ 1 + \exp(\mu - H)/kT \right]; \]  \hspace{1cm} (43)

we have from (42), for the variation in the free energy due to the vacancy

\[ \Delta F = -kT \log \left[ \left[ 1 + \exp(\mu - \omega)/kT \right] \left[ 1 + \exp(\mu - 2\beta - \omega)/kT \right]^{-1/2} \left[ 1 + \exp(\mu + 2\beta - \omega)/kT \right]^{-1/2} \right], \]  \hspace{1cm} (44)

or turning back to the inertial energy units of equation (23)

\[ \Delta F = -kT \log \left( \sqrt{2} \exp(\varepsilon/2kT) \cosh(\mu/2kT) \cosh((\mu - \varepsilon)/kT) + \cosh(2\beta/kT)^{-1/2} \right) \]  \hspace{1cm} (45)

it should be straightforward to obtain other thermodynamic functions in the same way.


Now, as a second example, we consider a one-band, nearest-neighbour, tight-binding model of a simple cubic semi-infinite crystal, which is obtained from the infinite periodic crystal by breaking the bonds between the atoms of two adjacent planes. The calculation is non self-consistent, but very simple analytical expressions are derived for the main physical properties of the crystal, which illuminate the fundamental properties of an ideal surface.

Shifting the origin of the energy to eliminate the constant diagonal matrix elements and changing the scale, the Hamiltonian of the one-dimensional lattice with one broken bond between sites 0 and 1 can be represented by the \( N \times N \) matrix

\[ H_1 = (I - D_0) m_1 + m_{-1}(I - D_0). \]  \hspace{1cm} (46)

The SC crystal with broken bonds between two neighbouring planes (100) can be described by the \( N^3 \times N^3 \) matrix

\[ H_S = I \otimes I \otimes H_1 + I \otimes M_1 \otimes I + M_1 \otimes I \otimes I, \]  \hspace{1cm} (47)

where \( M_1 \) has been defined in (6). As the matrix terms in the sum (47) commute, we have

\[ H_S^g = \sum_{p_1, p_2, p_3} \frac{p_1}{p_2} \frac{p_2}{p_3} M_{p_1} \otimes M_{p_2} \otimes H_1. \]  \hspace{1cm} (48)

So that taking into account equations (13), (14) and (5) is obtained the matrix function expression (where the limit \( N \to \infty \) is implied)

\[ f(H_S) = \sum_{q_1, q_2, q_3 = 0}^{N-1} \left< f(x_1 + x_2 + x_3), C_{q_1}(x_1) C_{q_2}(x_2) C_{q_3}(x_3) \right> \otimes M_{q_1} \otimes M_{q_2} \otimes C_{q_3}(H_1), \]  \hspace{1cm} (49)

which can be transformed by substitution of explicit expressions for Chebyshev's polynomials of the matrix. Obviously, we have

\[ C_0(H_1) = 2I, \]  \hspace{1cm} (50)

then by using the rules (2, 3, 4 ; 8 ; 18-22) of section 1, are easily found after some algebra the recurrence relations satisfied by the Chebyshev polynomials of even and odd order respectively

\[ C_{2p}(H_1) = -(D_p + D_{-p+1}) - (D_{p-1} + D_{-p}) m_2 - m_{-2}(D_{p-1} + D_{-p}) - \cdots + \]  \hspace{1cm} (51)

\[ + \left( I - \sum_{k=0}^{2p-1} D_{-k} \right) m_{2p} + m_{-2p} \left( I - \sum_{k=0}^{2p-1} D_{-k} \right), \]

\[ C_{2p+1}(H_1) = -(D_p + D_{-p}) m_1 - m_{-1}(D_p + D_{-p}) - (D_{p-1} + D_{-p-1}) m_3 - m_{-3}(D_{p-1} + D_{-p-1}) - \cdots + \]  \hspace{1cm} (52)

\[ + \left( I - \sum_{k=0}^{2p} D_{-k} \right) m_{2p+1} + m_{-2p-1} \left( I - \sum_{k=0}^{2p} D_{-k} \right). \]
The first order terms in those expressions, which are subsequently used, are checked by recurrence in appendix B.

Now substitution of equations (50, 51, 52) into equation (49) yields the following general expression

\[
f(H_g) = \sum_{q_2, q_3=0}^{N-1} \langle f(x_1 + x_2 + x_3), C_0(x_1) C_{q_2}(x_2) C_{q_3}(x_3) \rangle M_{q_2} \otimes M_{q_3} \otimes 2 \mathbf{I} -
\]

\[
- \sum_{q_1=1}^{N-1} \sum_{q_2, q_3=0}^{N-1} \langle f(x_1 + x_2 + x_3), C_{2q_1}(x_1) C_{q_2}(x_2) C_{q_3}(x_3) \rangle M_{q_1} \otimes M_{q_3} \otimes (D_{q_1} + D_{-q_1+1})
\]

\[
+ \sum_{q_1=1}^{N-1} \sum_{q_2, q_3=0}^{N-1} \langle f(x_1 + x_2 + x_3), C_{q_1}(x_1) C_{q_2}(x_2) C_{q_3}(x_3) \rangle M_{q_1} \otimes M_{q_2} \otimes (M_1 - D_0 m_1 - m_{-1} D_0)
\]

\[
- \sum_{q_1=1}^{N-1} \sum_{q_2, q_3=0}^{N-1} \langle f(x_1 + x_2 + x_3), C_{2q_1+1}(x_1) C_{q_2}(x_2) C_{q_3}(x_3) \rangle M_{q_1} \otimes M_{q_2}
\]

\[
\otimes [M_{q_1} + D_{-q_1}] m_1 + m_{-1}(D_{q_1} + D_{-q_1})] + \cdots,
\]

(53)

where, for simplicity, we have just written the first off-diagonal elements of the non-cyclic blocks. From this expression follow readily the elements of the matrix Green's function

\[
G(z) = (z - H_g)^{-1}, \quad (54)
\]

in the form

\[
G(000, 000; z) = 8 \langle (z - x_1 - x_2 - x_3)^{-1}, C_0(x_1) C_0(x_2) C_0(x_3) \rangle
\]

\[
= \frac{1}{64} \int_{0}^{2\pi} \int_{0}^{\pi} \int_{0}^{\pi} \sin^2 \theta_1 \sin \theta_2 \sin \theta_3 \mathrm{d}\theta_1 \mathrm{d}\theta_2 \mathrm{d}\theta_3
\]

(55)

\[
G(l00, 000; z) = 4 \langle (z - x_1 - x_2 - x_3)^{-1}, (2 C_0(x_1) - C_2(x_1)) C_0(x_2) C_0(x_3) \rangle, \quad (l \neq 0)
\]

\[
= \frac{2}{\pi^3} \int_{0}^{\pi} \int_{0}^{\pi} \int_{0}^{\pi} \frac{\sin^2 \theta_1 \sin \theta_2 \sin \theta_3}{(z - 2 \cos \theta_1 - 2 \cos \theta_2 - 2 \cos \theta_3)^{-1}} \mathrm{d}\theta_1 \mathrm{d}\theta_2 \mathrm{d}\theta_3
\]

(56)

\[
G(l' l'' l''', z) = G(l00, 000; z),
\]

(57)

for the diagonal elements.

Moreover, any interesting off-diagonal element of the matrix Green's function can also be easily obtained from (53), as for example

\[
G(0l_1 l_2, l_3 + 1l_1' l_2' l_3'; z) = 0
\]

\[
G(l_1 l_2 l_3, l_1 + 1l_2' l_3' l_3'; z) = \langle (z - x_1 - x_2 - x_3)^{-1}, (C_1(x_1) - C_{2l_1+1}(x_1)) C_{l_1-1}(x_2) C_{l_1-1}(x_3) \rangle =
\]

\[
= \frac{1}{\pi^3} \int_{0}^{\pi} \int_{0}^{\pi} \int_{0}^{\pi} \frac{[\cos \theta_1 - \cos (2l_1 + 1) \theta_1] \cos (l_2' - l_2) \cos (l_3' - l_3) \theta_3}{z - 2 \cos \theta_1 - 2 \cos \theta_2 - 2 \cos \theta_3} \mathrm{d}\theta_1 \mathrm{d}\theta_2 \mathrm{d}\theta_3
\]

(59)

for \( l \neq 0; \ldots \)

Denote the local density of states per site for the two and three dimensional perfect crystal respectively as \( v_3(E) \) and \( v_2(E) \); then, in the present case, from equations (55) and (56) and definition (33), the local density of states is

\[
n_{000}(E) = v_3(E),
\]

\[
n_{000}(E) = v_3(E) - 4 \langle \delta(E - x_1 - x_2 - x_3), C_2(x_1) C_0(x_2) C_0(x_3) \rangle.
\]

(60)

(61)

Whereas the total density of states is obtained by summing the above expressions in the form

\[
N^{-2} n(E) = N v_3(E) + 8 \langle \delta(E - x_1 - x_2 - x_3), C_0(x_1) C_0(x_2) C_0(x_3) \rangle -
\]

\[
- 8 \sum_{l=0}^{N-1/2} \langle \delta(E - x_1 - x_2 - x_3), C_2(x_1) C_0(x_2) C_0(x_3) \rangle,
\]

(62)

which, by virtue of equation (17) can be rewritten as

\[
N^{-2} n(E) = (N + 1) v_3(E) - 2 \langle \delta(E + 2 - x_2 - x_3) + \delta(E - 2 - x_2 - x_3), C_0(x_2) C_0(x_3) \rangle =
\]

\[
= (N + 1) v_3(E) - \left[ v_2(E + 2) + v_2(E - 2) \right]/2.
\]

(63)
Considering this exact expression of the density of states, the influence of the surface shows up obviously. The total number of states is easily checked to be equal to $N^3$, and no new state appears outside the three-dimensional band. In fact, the distribution of the new states is just the sum of a positive 3d-band and two negative translated 2d-bands. The Van Hove singularities being more pronounced in the 2d than in the 3d spectrum, and due to the coincidence of the singularities in $v_2(E)$ and $v_2(E \pm 2)$, it follows that the presence of the surface tends to erase the characteristic singularities of the 3d-spectrum at $E = \pm 2$ and $E = \pm 6$ (band edges).

Following the same line of argument as in section 3, the variation in the thermodynamic functions can be easily obtained. Considering, from equation (53),

$$\text{Tr } f(H_0) = \langle f(x_1 + x_2 + x_3), C_0(x_1) C_0(x_2) C_0(x_3) \rangle \cdot 8 N^3 - \sum_{q_1=1}^{(N-1)/2} \langle f(x_1 + x_2 + x_3), C_{2q_1}(x_1) C_0(x_2) C_0(x_3) \rangle \cdot 8 N^2,$$

we have, by taking equation (17), into account

$$\text{Tr } f(H_0) = 8 N^2(N + 1) \langle f(x_1 + x_2 + x_3), C_0(x_1) C_0(x_2) C_0(x_3) \rangle = -2 N^2 \langle f(2 + x_2 + x_3) + f(-2 + x_2 + x_3), C_0(x_2) C_0(x_3) \rangle,$$

from which follows, for example, the variation of the free energy $\Delta F$ due to the presence of the surface, with respect to the periodic crystal's free energy $F$ as

$$\Delta F = N^{-1} F - \frac{N^2}{2 \pi^2} \int_0^{\pi} \log \left[ 1 + \exp(\mu - 2 - 2 \cos \theta_1 - 2 \cos \theta_2) \right] \cdot$$

$$\left[ 1 + \exp(\mu + 2 - 2 \cos \theta_1 - 2 \cos \theta_2) \right] d\theta_1 d\theta_2,$$

with $\mu$ expressed in the same units as $H_1$ in equation (46).

5. Conclusion.

The main objective of the present paper was to demonstrate the ability of the FIGCM method to deal with crystals, exhibiting limited lack of periodicity, in the most natural and rigorous way; consequently the obtained results have only been briefly discussed here. But the characteristic of analytic formulae is to be self-explanatory; the displacements of the spectral weight due to the defect has been clearly stated, whereas the answers to other important questions concerning, for example, the localization and the charge transfers are given by the expressions of the Green's function elements, and will be analysed elsewhere. Moreover, it is clear from the treated example of the free-energy calculation that the determination of the density of states is not a necessary prerequisite to obtain the global physical properties of interest in closed form, by this method.

From these results, cyclic matrices appear to show more flexibility than Bloch's waves to be perturbed by defects. This property is worth being fully exploited in future by considering, for example, self-consistent treatments, high defect concentrations, ...

Appendix A.

Here, our purpose is to prove the validity of the lower order terms of the recurrence relations (26) and (27), which are used in the main text.

First making use of equations (2), (3), (4); (20), (21), (22) we find

$$C_2(H) = H^2 - 2 I$$

$$=(\alpha^2 - 2) D_0 - D_1 - D_{-1} + (I - D_0 - D_{-1} - D_{-2}) m_2 + m_{-2}(I - D_0 - D_{-1} - D_{-2}). \quad (A.1)$$

Dropping irrelevance terms of order $p > 2$, we have successively

$$C_2(H) C_{2p}(H) = \left[ C_2(\alpha) D_0 - D_1 - D_{-1} + (I - D_0 - D_{-1} - D_{-2}) m_2 + m_{-2}(I - D_0 - D_{-1} - D_{-2}) \right] \times \left[ C_{2p}(\alpha) D_0 - D_p - D_{-p} - (D_{p-1} + D_{p-1}) m_2 - m_{-2}(D_{p-1} + D_{p-1}) \right] - \cdots$$

$$= C_2(\alpha) C_{2p}(\alpha) D_0 - D_{p-1} - D_{-p-1} - m_{-2}(D_{p-1} + D_{p-1}) m_2 + \cdots$$

$$= C_2(\alpha) C_{2p}(\alpha) D_0 - D_{p-1} - D_{-p-1} - D_{p+1} - D_{-p+1} + \cdots. \quad (A.3)$$
and from equation (26) we have
\[ C_{2p-2}(H) = C_{2p-2}(x) D_0 - D_{p-1} - D_{-p+1} - \cdots \]  
(A.4)

substituting equations (A.2, A.3) in equation (8), we finally find
\[ C_{2p+2}(H) = C_{2p+2}(x) D_0 - D_{p+1} - D_{-p-1} + \cdots \]  
(A.5)
as required.
Considering now the Chebyshev polynomials of odd order, we have to check the following formula
\[ C_{2p+1}(H) = C_{2p+1}(x) D_0 - (D_p + D_{-p-1}) m_1 - m_{-1}(D_p + D_{-p-1}) - (D_{p-1} + D_{-p-2}) m_3 - m_{-3}(D_{p-1} + D_{-p-2}) - \cdots, \quad (p > 0) \]  
(A.6)
by recurrence, so we first calculate
\[
C_2(H) C_{2p+1}(H) = C_2(x) C_{2p+1}(x) D_0 - m_{-2}(I - D_0 - D_{-1} - D_{-2})(D_p + D_{-p-1}) m_1
- (I - D_0 - D_{-1} - D_{-2}) m_1(D_p + D_{-p-1}) - m_{-2}(I - D_0 - D_{-1} - D_{-2})(D_{p-1} + D_{-p-2}) m_3
- (I - D_0 - D_{-1} - D_{-2}) m_{-1}(D_{p-1} + D_{-p-2}) - \cdots
= C_2(x) C_{2p+1}(x) D_0 - m_{-2}(D_p + D_{-p-1}) m_1
- (I - D_0 - D_{-1} - D_{-2}) (D_{p-1} + D_{-p-2}) m_1
-m_{-2}(D_{p-1} + D_{-p-2}) m_3 - m_{-1}(I - D_{-1} - D_{-2} - D_{-3})(D_{p-1} + D_{-p-2}) - \cdots
= C_2(x) C_{2p+1}(x) D_0 - (D_{-p-2} + D_{p-1} + D_{-p} + D_{p+1}) m_1
-m_{-1}(D_{-p-2} + D_{p-1} + D_{-p} + D_{p+1}) - \cdots; \tag{A.7}
\]
and from equation (27) we have
\[ C_{2p-1}(H) = C_{2p-1}(x) D_0 - (D_{p-1} + D_{-p}) m_1 - m_{-1}(D_{p-1} + D_{-p}) - \cdots. \]  
(A.8)
Substituting equations (A.7, A.8) in equation (8), we finally obtain
\[ C_{2p+3}(H) = C_{2p+3}(x) D_0 - (D_{p+1} + D_{-p-2}) m_1 - m_{-1}(D_{p+1} + D_{-p-2}) - \cdots \]  
(A.9)
as required.

**Appendix B.**

To prove that the diagonal elements of the matrix (51) are correct, we first calculate
\[ C_2(H_1) = H_1^2 - 2 I = -(D_1 + D_0) - (D_0 + D_{-1}) m_2 - m_{-2}(D_0 + D_{-1}) + m_2 + m_{-2} \]  
(B.1)
then evaluating the diagonal elements of the matrix
\[
C_2(H_1) C_2(H_1) = \left[ -(D_1 + D_0) - (D_0 + D_{-1}) m_2 - m_{-2}(D_0 + D_{-1}) + m_2 + m_{-2} \right]
\times \left[ -(D_p + D_{-p-1}) - (D_{p-1} + D_{-p}) m_2 - m_{-2}(D_{p-1} + D_{-p}) - \cdots \right]
= -(m_2 + m_{-2}) [(D_{p-1} + D_{-p}) m_2 + m_{-2}(D_{p-1} + D_{-p}) - \cdots]
\]
\[ C_2(H_1) C_2(H_1) = -(D_{p-1} + D_{-p}) m_2 - \cdots \]
\[ = -(D_{p-1} + D_{-p} + D_{p+1} + D_{-p+2}) - \cdots, \tag{B.2}
\]
and getting
\[ C_{2p-2}(H_1) = -(D_{p-1} + D_{-p+2}) - \cdots \]  
(B.3)
from equation (51), we have by substituting equations (B.2) and (B.3) in equation (8)
\[ C_{2p+2}(H_1) = -(D_{p+1} + D_{-p}) - \cdots \]  
(B.4)
as required.
Let us now check the first off-diagonal elements of the matrix (52), by considering first

\[ C_2(H_1) C_{2p+1}(H_1) = \left[ - (D_1 + D_0) - (D_0 + D_{-1}) m_2 - m_{-2}(D_0 + D_{-1}) + m_2 + m_{-2} \right] \times \left[ - (D_p + D_{-p}) m_1 - m_{-1}(D_p + D_{-p}) - (D_p-1 + D_{-p-1}) m_3 - m_{-3}(D_p-1 + D_{-p-1}) \right] \]

\[ = - m_{-2}(D_p + D_{-p}) m_1 - m_{1}(D_p + D_{-p}) \]

\[ - m_{-2}(D_{p-1} + D_{-p-1}) m_3 - m_{-1}(D_{p-1} + D_{-p-1}) - \cdots \]

\[ = - m_{-1}(D_{p+1} + D_{-p+1} - D_{p-1} - D_{-p-1}) - (D_{p-1} + D_{-p-1} + D_{p+1} + D_{-p+1}) - \cdots \]

and then

\[ C_{2p-1}(H_1) = - (D_{p-1} + D_{-p+1}) m_1 - m_{-1}(D_{p-1} + D_{-p+1}) - \cdots, \]

\[ C_{2p+3}(H_1) = - (D_{p+1} + D_{-p-1}) m_1 - m_{-1}(D_{p+1} + D_{-p-1}) - \cdots \]

which completes the proof by recurrence.

References