Highly convergent schemes for the calculation of bulk and surface Green functions

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Abstract. The surface and bulk densities of states of a solid described by the stacking of principal layers are obtained by means of an iterative procedure which allows (i) the inclusion of 2^n layers after n iterations, (ii) the simultaneous calculation of the Green functions for both the 'right' and 'left' surfaces as well as for the bulk (or central) principal layer, and (iii) the use of imaginary parts η as small as one wishes in the energy without any large increase in computing time, so that the limit $\eta \to 0$ can really be obtained. As a by-product we obtain (i) the 'right' and 'left' transfer matrices of the 'effective field' or continuous fraction approach and (ii) a factorisation theorem which relates the Green functions of both surfaces to the Green functions of the bulk and the free metal atom.

1. Introduction

Recently a large number of papers have appeared where different kinds of Green functions are calculated by one of the several iterative methods available (Cyrot Lackmann 1970, Haydock *et al* 1972, Anishchik *et al* 1976, Mele and Joannopoulos 1978). One of the most popular is the 'effective field' or transfer matrix approach (Falicov and Yndurain 1975, Lee and Joannopoulos 1981a, b). Most of them have in common a relatively slow convergence, particularly near singularities (Dy *et al* 1979, Lee and Joannopoulos 1981a, b). This problem has been touched upon in two recent publications (Guinea *et al* 1983, López Sancho *et al* 1984) which propose iterative schemes quicker than the usual one in the transfer matrix approach. One of them (Guinea *et al* 1983) aims at obtaining effective interactions for two-dimensional Hamiltonians at surfaces by means of decimation techniques, while the other (López Sancho *et al* 1984) presents a quick iterative method for the calculation of the transfer matrix so as to save computation time in the calculation of densities of states. Although the two approaches seem different at first sight, they really correspond to different versions of a general scheme for quick convergence of iterative processes, ultimately related to the renormalisation-group method (Gonçalves da Silva and Keiller 1981).

In this paper, decimation techniques are reformulated with the help of the effective-layer concept. We take as an illustrative example the problem of solving the conventional linear chain of equations for the matrix elements of the Green operator $G(\omega) = (\omega - H)^{-1}$ in a basis of localised functions. The method involves replacing the original chain by an effective one of twice the lattice constant, where each layer plus its two nearest neighbours in the original chain are replaced by an effective layer in the new chain; these effective layers interact through energy-dependent residual interactions which are weaker than those

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of the original chain. This replacement can be repeated iteratively until the residual interactions between effective layers are as small as one wishes. After n iterations, say, one has a chain of lattice constant 2^n times the original one, each effective layer replacing 2^n original layers. The effective interlayer interactions become vanishingly small after a few iterations (usually five or six for $\eta = 10^{-2}$ Ryd). Note that each new iteration doubles the number of original layers included in the new effective layer. This is where the big advantage of the method lies, making it extremely powerful just in those situations where conventional iteration methods converge so slowly as to become almost hopeless. For instance, small η values (e.g. 10^{-5} Ryd) require 12–14 iterations, i.e. about 2.5 times the iterations needed for $\eta = 10^{-2}$ Ryd. To get the same accuracy, 2^{12}–2^{14} (4096–16384) iterations would be required in the conventional T-matrix approach!

The format of this paper is as follows. The effective chain is introduced in § 2, followed by the iterative procedure which allows us to obtain effective chains with successively weaker residual interactions. This leads to expressions for the Green functions for the 'right' and 'left' surfaces as well as for the bulk, which can be computed rather efficiently. Section 3 establishes a connection with usual T-matrix approaches and ends with recurrence formulae for matrix elements involving inner layers. Section 4 starts with the tight-binding version of the factorisation theorem which serves to link with other approaches like the matching Green function method (Garcia-Moliner and Rubio 1969, 1971, Inglesfield 1971) and discusses some unclear points about surface boundary conditions. Finally, some concluding remarks are made in § 5.

2. Effective layers

As is well known (Lee and Joannopoulos 1981a), any solid with a surface can be described by a semi-infinite stack of principal layers with nearest-neighbour interactions. If the bulk periodicity on the surface plane is preserved by all the atomic planes right up to the surface, then k is a good quantum number and we can build Bloch-state orbitals for each atomic orbital ϕ_α along any atomic plane, for example the λth atomic plane of the nth principal layer. Take m orbitals per atom and suppose each principal layer is composed of l atomic planes. Then one can form column-vector Bloch states for each principal layer:

$$\Psi_n(\boldsymbol{k}_\parallel) = \begin{pmatrix} \varphi_n^{11}(\boldsymbol{k}_\parallel) \\ \vdots \\ \varphi_n^{\lambda\alpha}(\boldsymbol{k}_\parallel) \\ \vdots \\ \varphi_n^{lm}(\boldsymbol{k}_\parallel) \end{pmatrix} \tag{1}$$

where

$$\varphi_n^{\lambda\alpha}(\boldsymbol{k}_\parallel) = \frac{1}{\sqrt{N_\parallel}} \sum_{\boldsymbol{R}_\parallel} \exp(\mathrm{i}\boldsymbol{k}_\parallel \boldsymbol{R}_\parallel)\phi_n^{\lambda\alpha}(\boldsymbol{R}_\parallel) \tag{2}$$

and $N_\parallel$ and $\boldsymbol{R}_\parallel$ denote the numbers of atoms and lattice vectors in an atomic plane.

Taking matrix elements of $(\omega - H)G(\omega) = \mathscr{I}$ between the Bloch states (2), one has the usual chain for each $\boldsymbol{k}_\parallel$:

$$\begin{aligned}
(\omega - H_{00})G_{00} &= I + H_{01}G_{10} \\
(\omega - H_{00})G_{10} &= H_{01}^+ G_{00} + H_{01}G_{20} \\
&\ \vdots \\
(\omega - H_{00})G_{n0} &= H_{01}^+ G_{n-1,0} + H_{01}G_{n+1,0}
\end{aligned} \tag{3}$$

where $n = 0$ denotes the surface principal layer and the matrices

$$H_{nn'}(\boldsymbol{k}_{\|}) = \langle \Psi_n(\boldsymbol{k}_{\|}) | H | \Psi_{n'}(\boldsymbol{k}_{\|}) \rangle,$$

$$G_{nn'}(\omega, \boldsymbol{k}_{\|}) = \langle \Psi_n(\boldsymbol{k}_{\|}) | G(\omega) | \Psi_{n'}(\boldsymbol{k}_{\|}) \rangle \tag{4}$$

and I (the unit matrix) are of rank $l \times m$. In equation (3) we have made the simplifying but not essential assumption of an ideal surface, i.e., $H_{00} = H_{11} = \ldots$ and $H_{01} = H_{12} = \ldots$. Now we are in a position to discuss the method of effective layers.

From the general term in (3), one has

$$G_{n0}(\omega) = (\omega - H_{00})^{-1}(H_{01}^+ G_{n-1,0} + H_{01} G_{n+1,0}) \qquad (n \geqslant 1). \tag{5}$$

Put $n = 1$ into this equation and put the result into the first equation of the chain (3). This yields

$$[\omega - H_{00} - H_{01}(\omega - H_{00})^{-1}H_{01}^+]G_{00} = I + H_{01}(\omega - H_{00})^{-1}H_{01} G_{20}, \tag{6}$$

which relates G_{00} to G_{20}. Likewise, consider the general equation of the chain, equation (5), and replace $G_{n-1,0}$ and $G_{n+1,0}$ after equations (3). One gets

$$[\omega - H_{00} - H_{01}(\omega - H_{00})^{-1}H_{01}^+ - H_{01}^+(\omega - H_{00})^{-1}H_{01}]G_{n0}$$

$$= H_{01}^+(\omega - H_{00})^{-1}H_{01}^+ G_{n-2,0} + H_{01}(\omega - H_{00})^{-1}H_{01} G_{n+2,0} \qquad (n \geqslant 2). \tag{7}$$

Nearest neighbours have disappeared in equations (6) and (7). These equations can be rewritten more compactly as

$$(\omega - \varepsilon_{1s})G_{00} = I + \alpha_1 G_{20}$$

$$(\omega - \varepsilon_1)G_{n0} = \beta_1 G_{n-2,0} + \alpha_1 G_{n+2,0} \qquad (n \geqslant 2) \tag{8}$$

$$(\omega - \varepsilon_1)G_{nn} = I + \beta_1 G_{n-2,n} + \alpha_1 G_{n+2,n}$$

with

$$\alpha_1 = H_{01}(\omega - H_{00})^{-1}H_{01}$$

$$\beta_1 = H_{01}^+(\omega - H_{00})^{-1}H_{01}^+$$

$$\varepsilon_{1s} = H_{00} + H_{01}(\omega - H_{00})^{-1}H_{01}^+ \tag{9}$$

$$\varepsilon_1 = H_{00} + H_{01}(\omega - H_{00})^{-1}H_{01}^+ + H_{01}^+(\omega - H_{00})^{-1}H_{01}.$$

Now, consider the subset formed by taking only even values for n in (8), i.e.,

$$(\omega - \varepsilon_{1s})G_{00} = I + \alpha_1 G_{20}$$

$$(\omega - \varepsilon_1)G_{2n,0} = \beta_1 G_{2(n-1),0} + \alpha_1 G_{2(n+1),0} \tag{10}$$

$$(\omega - \varepsilon_1)G_{2n,2n} = I + \beta_1 G_{2(n-1),2n} + \alpha_1 G_{2(n+1),2n}.$$

These equations define a chain which couples the Green-function matrix elements with even indices only, $G_{2n,0}$, through effective nearest-neighbour interactions given by the first two equations of (9) and with effective zeroth-order matrix elements already different for the surface (ε_{1s}) and the inner layers (ε_1). Equations (9) define an effective Hamiltonian describing a chain of effective layers of lattice constant $2a$, twice the original one. Each effective layer contains implicitly the effect of its nearest neighbours in the original chain (through the use of equation (5)).

Except for the different zeroth-order matrix elements, $\varepsilon_{1s} \neq \varepsilon_1$, equations (10) are isomorphic to equations (3). Therefore, the argument going from (3) to (10) can be repeated if we start from (10). Repeating the argument i times, we have the iterative sequence

$$
\begin{aligned}
\alpha_i &= \alpha_{i-1}(\omega - \varepsilon_{i-1})^{-1}\alpha_{i-1} \\
\beta_i &= \beta_{i-1}(\omega - \varepsilon_{i-1})^{-1}\beta_{i-1} \\
\varepsilon_i &= \varepsilon_{i-1} + \alpha_{i-1}(\omega - \varepsilon_{i-1})^{-1}\beta_{i-1} + \beta_{i-1}(\omega - \varepsilon_{i-1})^{-1}\alpha_{i-1} \\
\varepsilon_i^s &= \varepsilon_{i-1}^s + \alpha_{i-1}(\omega - \varepsilon_{i-1})^{-1}\beta_{i-1},
\end{aligned}
\tag{11}
$$

starting with $\varepsilon_0 = H_{00}$, $\alpha_0 = H_{01}$ and $\beta_0 = H_{01}^+$. Equations (11) define an effective Hamiltonian (Guinea *et al* 1983) for a chain of lattice constant $2^i a$ with nearest-neighbour interactions α_i and β_i and zeroth-order Hamiltonian matrix elements ε_i and ε_i^s. After i iterations

$$
\begin{aligned}
(\omega - \varepsilon_i^s)G_{00} &= I + \alpha_i G_{2^i n, 0} \\
(\omega - \varepsilon_i)G_{2^i n, 0} &= \beta_i G_{2^i(n-1), 0} + \alpha_i G_{2^i(n+1), 0}
\end{aligned}
\qquad (n \geqslant 1).
\tag{12}
$$

Each layer of the ith chain contains implicitly the effect of the nearest neighbours of the previous chain $(i-1)$. After ν iterations, the zeroth layer is equivalent to the orginal zeroth layer coupled to 2^ν layers, while any inner layer contains $2^{n+1} - 1$ layers of the orginal chain. The iteration is to be repeated until α_ν and β_ν are as small as one wishes. Then clearly $\varepsilon_\nu \simeq \varepsilon_{\nu-1}$, $\varepsilon_\nu^s \simeq \varepsilon_{\nu-1}^s$ and

$$
\begin{aligned}
(\omega - \varepsilon_\nu^s)G_{00} &\simeq I \\
(\omega - \varepsilon_\nu)G_{2^\nu n, 2^\nu n} &\simeq I \qquad (n \geqslant 1).
\end{aligned}
\tag{13}
$$

Therefore, we have obtained as good an approximation as we wished for G_{00},

$$
G_{00}(\omega) \simeq (\omega - \varepsilon_\nu^s)^{-1}
\tag{14}
$$

and for $G_{nn}(n \to \infty) \equiv G_b$, the Green function for the bulk layer. Since the second equation in (13) does not depend on n, we obviously have

$$
\lim_{n \to \infty} G_{nn} = G_{2^\nu, 2^\nu} \simeq (\omega - \varepsilon_\nu)^{-1} \equiv G_b.
\tag{15}
$$

The Green function for the dual surface, i.e. for the zeroth layer of the complementary chain, can be clearly obtained by exchanging α_i and β_i:

$$
\bar{G}_{00} = (\omega - \bar{\varepsilon}_\nu)^{-1}
\tag{16}
$$

where $\bar{\varepsilon}_\nu^s$ is obtained by iterating

$$
\bar{\varepsilon}_{i+1}^s = \bar{\varepsilon}_i^s + \beta_i(\omega - \varepsilon_i)^{-1}\alpha_i,
\tag{17}
$$

starting with $\varepsilon_0 = \bar{\varepsilon}_0^s = H_{00}$, $\alpha_0 = H_{01}$ and $\beta_0 = H_{01}^+$, as before, until $\varepsilon_\nu^s \simeq \bar{\varepsilon}_{\nu-1}^s$.

It should be noticed that the iterative procedure presented here is exact in the sense that no interactions are omitted in a nearest-neighbour chain. This does not imply any special restriction because any chain of atoms with any (one-body) interactions can be reduced to a chain with nearest-neighbour interactions by the use of the principal-layer concept.

3. Recurrence relations for matrix elements involving inner layers: T and $\bar{T}$ matrices

Equations (14) and (16) thus give the Green functions for the two complementary surfaces, sometimes called the 'right' and 'left' surfaces, whereas equation (15) gives the Green function for the 'bulk' or 'central' layer of an infinite crystal. Once G_{00} and $\bar{G}_{00}$ are known, all the matrix elements of G can be obtained trivially.

3.1. T matrices

Take the general term in equation (3). Applying the effective-layer argument to $G_{n+1,0}$ only, we have after ν iterations

$$(\omega - \varepsilon_\nu^!)G_{n,0} = H_{01}^+ G_{n-1,0} + \alpha_\nu G_{n+2\nu,0} = H_{01}^+ G_{n-1,0}$$

since $\alpha_\nu \simeq 0$, i.e.,

$$G_{n,0} = (\omega - \varepsilon_\nu^!)^{-1} H_{01}^+ G_{n-1,0} \equiv G_{00} H_{01}^+ G_{n-1,0} \qquad (n \geqslant 1) \qquad (18)$$

or

$$T = G_{00} H_{01}^+, \qquad (19)$$

which is just the well known expression (Haydock *et al* 1972, Anishchik *et al* 1976, Mele and Joannopoulos 1978) for the transfer matrix of the crystal in the forward direction $(n \to n+1)$. Similarly, exchanging α_ν and β_ν, we get the transfer matrix for the complementary chain (negative n)

$$G_{\bar{n},0} = (\omega - \bar{\varepsilon}_\nu^s)^{-1} H_{01} G_{\bar{n}+1,0} \qquad (\bar{n} \leqslant -1), \qquad (20)$$

i.e.,

$$\bar{T} = (\omega - \bar{\varepsilon}_\nu^s)^{-1} H_{01} = \bar{G}_{00} H_{01}. \qquad (21)$$

If the two complementary chains are joined together to reconstruct the bulk crystal, T and $\bar{T}$ serve to run through the crystal along the forward (increasing n) or backward (decreasing n) direction. Hence, if n is large enough to reach the bulk in the forward direction,

$$G_{n,0} = \bar{T} G_{n+1,0} \qquad n \to \infty. \qquad (22)$$

It should be stressed that, whereas equation (18) may be used for any $n \geqslant 1$ in a semi-infinite crystal, equation (22) may be used *only for large values of n*. Similarly, in the case of the complementary chain,

$$G_{\bar{n},0} = T G_{\bar{n}-1,0} \qquad \bar{n} \to -\infty. \qquad (23)$$

Finally, a relationship can be obtained which allows decreasing n for any $n \geqslant 1$. Simply notice that $G(\omega)$ satisfies $G(\omega)(\omega - H) = \mathscr{I}$ equally well. Hence we can write, instead of (18),

$$G_{0,n} = G_{0,n-1} H_{01} G_{00} \equiv G_{0,n-1} S \qquad (n \geqslant 1), \qquad (24)$$

which defines another transfer matrix, S.

Formulae (19) and (21) provide an iterative sequence for the calculation of T and $\bar{T}$, in contrast to the procedure given by López Sancho *et al* (1984) where a similar iterative scheme was developed to obtain T in the form of a series expansion. There, each new

iteration was added to the previous one, thus generating the expressions

$$T = t_0 + \tilde{t}_0 t_1 + \tilde{t}_0 \tilde{t}_1 t_2 + \ldots$$
$$\bar{T} = \tilde{t}_0 + t_0 \tilde{t}_1 + t_0 t_1 \tilde{t}_2 + \ldots \tag{25}$$

where

$$t_i = (I - t_{i-1}\tilde{t}_{i-1} - \tilde{t}_{i-1}t_{i-1})^{-1} t_{i-1}^2$$
$$\tilde{t}_i = (I - t_{i-1}\tilde{t}_{i-1} - \tilde{t}_{i-1}t_{i-1})^{-1} \tilde{t}_{i-1}^2$$

starting with

$$t_0 = (\omega - H_{00})^{-1} H_{01}^+$$
$$\tilde{t}_0 = (\omega - H_{00})^{-1} H_{01}.$$

3.2. Recurrence relations

From the last equation in (3) we have, after (18) and (24),

$$(\omega - H_{00} - H_{01}T)G_{nn} = I + H_{01}^+ G_{n-1,n} = I + H_{01}^+ G_{n-1,n-1}S \tag{26}$$

while, on the other hand, from the first equation in (3),

$$(\omega - H_{00} - H_{01}T)G_{00} = I. \tag{27}$$

Therefore

$$G_{nn} = G_{00} + G_{00}H_{01}^+ G_{n-1,n-1}S = G_{00} + TG_{n-1,n-1}S \qquad (n \geqslant 1) \tag{28}$$

which allows any diagonal matrix element of G to be obtained iteratively.

The Green function for the bulk layer can now be found trivially. Letting $n \to \infty$ in (24) and making use of (23), we obtain

$$(\omega - H_{00} - H_{01}T - H_{01}^+\bar{T})G_{nn} = I \qquad n \to \infty. \tag{29}$$

Therefore, from (15),

$$\varepsilon_\nu = H_{00} + H_{01}T + H_{01}^+\bar{T}, \tag{30}$$

whereas from (27) and (14),

$$\varepsilon_\nu^s = H_{00} + H_{01}T \tag{31}$$

and, similarly, v have for the dual surface

$$\bar{\varepsilon}_\nu^s = H_{00} + H_{01}^+\bar{T}. \tag{32}$$

4. The factorisation theorem

Equations (30)–(32) allow us to find a relationship between the three G and $(\omega - H_{00})^{-1} \equiv G_0$, the Green function of an isolated layer (the surface layer in fact). We can write

$$G_{00}^{-1} + \bar{G}_{00}^{-1} = G_b^{-1} + G_0^{-1} = G_b^{-1}(G_b + G_0)G_0^{-1}. \tag{33}$$

In particular, if the two surfaces are identical (the symmetric case), $G_{00} = \bar{G}_{00} = G_s$, and then

$$G_s^{-1} = \tfrac{1}{2}(G_b^{-1} + G_0^{-1}) = \tfrac{1}{2}G_b^{-1}(G_b + G_0)G_0^{-1}. \tag{34}$$

Equations (33) and (34) are indeed reminiscent of similar relationships which hold in the surface Green function method (García-Moliner and Rubio 1969, 1971, Inglesfield 1971) between the surface Green function and the bulk and vacuum Green functions. The novelty of equations (33)–(34) is that, instead of the vacuum Green function, one has the Green function for an isolated atom (layer). Matching with vacuum does not enter anywhere. This is simply traced to the way in which surfaces are usually introduced in the tight-binding approach, namely chopping off the interactions of the surface layer with the outside region because, one says, there are no atoms left. However, this is equivalent to placing an infinite barrier, thereby eliminating surface states from the picture due to matching. In other words, although there are no atoms left outside the crystal, one still has the kinetic energy, so that, instead of $G_0 = (\omega - H_{00})^{-1}$, the bound part, one should have the complete atom (layer) Green function with its scattering states included. Recent attempts have been made to improve the tight-binding approach (Pollmann and Pantelides 1978, Krieger and Laufer 1981, Williams *et al* 1982, Schmeits *et al* 1983) but no complete answer has yet been given to the question of matching surface states within this approach. Work along this line is now going on and will be the subject of a forthcoming publication.

5. Conclusions

In summary, the iterative approach discussed above provides a powerful and quick way of evaluating different kinds of Green functions (right surface, left surface, bulk, etc). With the help of some recurrence relations, discussed in § 3, one can find all the matrix elements of the Green operator. A factorisation theorem, reminiscent of a similar relationship in the surface Green-function matching formalism, is evidence of a fundamental weakness in current treatments of surfaces by the tight-binding approach: surface states due to matching with a vacuum are not dealt with adequately, and thus we are restricted to an infinite-barrier situation.

References

Anishchik V, Falicov L M and Yndurain F 1976 *Surf. Sci.* **57** 375–84
Cyrot Lackmann F 1970 *J. Physique Suppl.* **35** C1 67–74
Dy K S, Wu Shi-Yu and Sprathn T 1979 *Phys. Rev.* B **20** 4237–43
Falicov L and Yndurain F 1975 *J. Phys. C: Solid State Phys.* **8** 147–57
Garcia-Moliner F and Rubio J 1969 *J. Phys. C: Solid State Phys.* **2** 1789–96
—— 1971 *Proc. R. Soc.* A **324** 257–73
Gonçalves da Silva C E T and Keiller B 1981 *Solid State Commun.* **40** 215–9
Guinea F, Tejedor C, Flores F and Lous E 1983 *Phys. Rev.* B **28** 4397–402
Haydock R, Heine V and Kelly M J 1972 *J. Phys. C: Solid State Phys.* **5** 2845–58
Inglesfield J E 1971 *J. Phys. C: Solid State Phys.* **4** L14–7
Krieger J B and Laufer P M 1981 *Phys. Rev.* B **23** 4063–75

Lee D H and Joannopoulos J D 1981a *Phys. Rev.* B **23** 4988–96
—— 1981b *Phys. Rev.* B **23** 4997–5004
López Sancho M P, López Sancho J M and Rubio J 1984 *J. Phys. F: Met. Phys.* **14** 1205–15
Mele E J and Joannopoulos J D 1978 *Phys. Rev.* B **17** 1816–27
Pollmann J and Pantelides S T 1978 *Phys. Rev.* B **18** 5524–44
Schmeits M, Mazur A and Pollmann J 1983 *Phys. Rev.* B **27** 5012–31
Williams A R, Feibelman P J and Lang N D 1982 *Phys. Rev.* B **26** 5433–44