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Methods of embedding for defect and surface problems

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Abstract. In the theory of defects and surfaces the solution for a small part of the solid is often all that is of interest. This paper considers the problem of finding within such a small subdomain or 'cluster' the correct solution to the equation of motion of the whole system. It is first shown how the 'embedding-potential' method of 'perturbed-cluster' theory is equivalent to the usual Green function methods of 'perturbed-crystal' theory. Then other 'perturbed-cluster' methods are considered and it is shown that, because of the further assumptions about the solution that are involved, they fail to remove properly some of the spurious features introduced by performing a cluster calculation. This is demonstrated by the solution of simple model systems. It is shown how the matrix elements of certain operators and the correct normalisation of the state function can be calculated from a solution in the cluster region only. Next it is shown that the real-space embedding procedure introduced by Inglesfield corresponds in a discrete basis to a fundamentally different way of calculating the embedding potential, which is especially suitable for use in surface problems. This too is illustrated with a simple example, and some implicit equations for the embedding potential that do not involve the Green function of the host crystal are derived for the case where different possible cluster boundaries are related by lattice symmetry operations. Finally the implementation of these schemes and the application of the ideas to other quantum problems involving subdomains are briefly considered.

1. Introduction

This paper addresses the solution of the equations of motion for a subdomain of a quantum system. It seeks to clarify the relationship between some methods that have been used in the theory of the electronic structures of defects in crystalline materials; to show why some are to be preferred to others; and to emphasise that the distinction between 'perturbed-crystal' methods (where the solution for the perfect solid is modified to account for the presence of the defect) and 'perturbed-cluster' methods (where the solution for a small region around the defect is modified to account for the presence of the rest of the crystal) derives from the order in which the computations are performed rather than from any difference of principle.

It will be tacitly assumed that the system may be described by some sort of 'effective single-particle Hamiltonian' (i.e. one quadratic in some renormalised field operators) and that the problem of the perfect crystal in the absence of the defect has been solved to some desired accuracy. The language of defect theory will be used throughout but

some other situations in which the methods considered are applicable are mentioned briefly.

A preliminary account of part of this work has already been given (Fisher 1987).

2. Single-particle formalism

2.1. Introduction to the matrix formalism: the Q operator and Green matrix

Suppose the system of interest may be sufficiently described by a (non-orthogonal) set of basis kets $\{|\varphi_i\rangle\}$ so that the problem may be stated in matrix form. For convenience in dealing with such a non-orthogonal basis we adopt a notation that enables the matrix relations to be written in a natural and unambiguous way. This notation was proposed by Ballentine and Kolář (1986), who urged that it be adopted as standard, and it has already gained wide acceptance among practitioners in the theory of electronic structure (see e.g. Foulkes and Haydock 1986, Sutton *et al* 1988). A dual basis set $\{|\varphi^i\rangle\}$ is defined by

$$|\varphi^i\rangle = \sum_j (S^{-1})^{ji} |\varphi_j\rangle \quad (1)$$

where

$$S_{ij} = \langle \varphi_i | \varphi_j \rangle \quad (2)$$

so that

$$\langle \varphi^i | \varphi_j \rangle = \delta_j^i. \quad (3)$$

Then a general ket may be expanded in either of the two sets

$$|u\rangle = \sum_i u^i |\varphi_i\rangle = \sum_i u_i |\varphi^i\rangle \quad (4)$$

and an operator \hat{O} may be represented in four different matrix forms: namely the 'upper form'

$$O^{ij} = \langle \varphi^i | \hat{O} | \varphi^j \rangle \quad (5)$$

the two 'mixed forms'

$$O_i^j = \langle \varphi^i | \hat{O} | \varphi_j \rangle \quad O_i^j = \langle \varphi_i | \hat{O} | \varphi^j \rangle \quad (6)$$

and the 'lower form'

$$O_{ij} = \langle \varphi_i | \hat{O} | \varphi_j \rangle. \quad (7)$$

Following Pisani (1978) the operator \hat{Q} is defined by

$$\hat{Q} = E\hat{I} - \hat{H} \quad (8)$$

where E is the energy, \hat{H} is the Hamiltonian and \hat{I} the identity operator. The Green matrix G is defined through

$$\sum_k Q_{ik} G^{kj} = \delta_i^j \quad (9)$$

i.e. as the upper representation of the Green function, which is the operator inverse of \hat{Q} .

2.2. The embedding potential

2.2.1. Perturbed-crystal derivation. Suppose the basis set is divided into two parts: the C (or 'cluster') region in which the Q matrix is altered from its value in the perfect crystal and the remaining region D in which the Q matrix is unaffected, so

$$Q_{CD} = Q_{CD}^0 \quad Q_{DD} = Q_{DD}^0. \quad (10)$$

Once this partition has been made, all the remaining manipulations in this section are purely formal and do not affect the physics of the system.

The fundamental equation of *perturbed-crystal* theory is the Dyson equation (see e.g. Stoneham 1975 p 105)

$$G^{CC} = G^{0CC} + G^{0CC} V_{CC} G^{CC} \quad (11)$$

where the superscript 0 always refers to the perfect crystal and V_{CC} is (minus) the difference between the CC blocks of the Q matrices in the defective and perfect crystals:

$$V_{CC} = -(Q_{CC} - Q_{CC}^0). \quad (12)$$

Note that V_{CC} here involves not only the change in the Hamiltonian matrix but also any alteration in the overlap matrix due to the choice of different orbitals to describe the perfect and defective crystals. Equations (11) and (12) may be rearranged to give

$$(G^{CC})^{-1} = Q_{CC} - Q_{CC}^0 + (G^{0CC})^{-1} \quad (13)$$

which is the *perturbed-cluster* equation of Baraff and Schlüter (1986). It states that the part of the Green matrix within the cluster may be obtained by inverting just the CC block of the Q matrix provided one adds to the Hamiltonian an energy-dependent *embedding potential*

$$\Sigma_{CC}(E) = Q_{CC}^0 - (G^{0CC})^{-1}. \quad (14)$$

The existence of such an effective potential has also been noted by other authors (e.g. Oswald *et al* 1985).

2.2.2. Perturbed-cluster derivation. One can obtain exactly the same result from the *perturbed-cluster* viewpoint. The Schrödinger equation may be written in the block matrix form

$$\begin{bmatrix} Q_{CC} & Q_{CD} \\ Q_D & Q_{DD} \end{bmatrix} \begin{bmatrix} \psi^C \\ \psi^D \end{bmatrix} = 0 \quad (15)$$

and the second row of this yields

$$Q_{DC}\psi^C + Q_{DD}\psi^D = 0. \quad (16)$$

This may be solved (Löwdin 1951) to give ψ^D in terms of ψ^C :

$$\psi^D = -(Q_{DD})^{-1} Q_{DC}\psi^C \quad (17)$$

and substituting in the first row,

$$[Q_{CC} - Q_{CD}(Q_{DD})^{-1}Q_{DC}]\psi^C = 0. \quad (18)$$

This is equivalent to solving the Schrödinger equation within the C region alone with an additional energy-dependent potential

$$\Sigma_{CC}(E) = Q_{CD}(Q_{DD})^{-1}Q_{DC}. \quad (19)$$

By assumption all the quantities on the right-hand side are unchanged between the perfect and defective crystals (see equation (10)) so

$$\Sigma_{CC}(E) = \Sigma_{CC}^0(E) \quad (20)$$

and in particular one can calculate Σ_{CC} given the cluster-projected perfect-crystal Green matrix

$$G^{0CC} = (Q_{CC}^0 - \Sigma_{CC}^0)^{-1} \quad (21)$$

which is clearly equivalent to the Baraff-Schlüter formula.

2.3. Properties of the embedding potential

In equation (19) it is easy to see that if the elements of the Hamiltonian and overlap matrices are only significant between 'nearby' orbitals then the embedding potential is a surface potential, having non-zero elements only between those states in the C region which have significant elements in the CD block of the Q matrix connecting them to the D region. Arbitrary changes can be made to the basis set in the centre of the cluster where the embedding potential is zero in order to describe the defect adequately; this is equivalent to the 'ad-space' method of basis expansion in perturbed-crystal theory described by Williams *et al* (1982). It is also clear that once the embedding potential has been calculated, it can be used for a variety of different defect problems which differ only in the CC block of the Q matrix.

Of course the Green functions have a branch cut along the real energy axis for all energies lying within a band of the bulk solid and the embedding potential must therefore be evaluated for complex energies. The density of states may be obtained from the imaginary part of the Green function by taking the limit where the imaginary part of the energy goes to zero, but it may be more convenient, if it is desired only to calculate the density matrix integrated over energy, to deform the contour of integration away from the real axis into the complex energy plane. This point is discussed further in § 10.

3. 'Corrective operator' methods

Other solutions of the embedding problem that have been proposed without reference to the perturbed-crystal formalism involve the assumption that some part of the Green matrix is unaltered on passing from the perfect to the defective crystal. This means that the physics of the system is altered to a degree that may be unacceptable in many applications. These solutions are considered in turn.

3.1. The multiplicative corrective operator over the entire cluster

A multiplicative corrective operator is used (Pisani 1978, 1985) to pass from the inverse of the Q matrix in the cluster region to the Green function within that region:

$$G^{CC} = J^C_C(Q_{CC})^{-1}. \quad (22)$$

The J matrix may be found from the matrix relation

$$\begin{bmatrix} G^{CC} & G^{CD} \\ G^{DC} & G^{DD} \end{bmatrix} \begin{bmatrix} Q_{CC} & Q_{CD} \\ Q_{DC} & Q_{DD} \end{bmatrix} = \begin{bmatrix} 1^C_C & 0 \\ 0 & 1^D_D \end{bmatrix} \quad (23)$$

which implies

$$G^{CC}Q_{CC} = 1^C_C - G^{CD}Q_{DC} \quad (24)$$

and therefore

$$J^C_C = 1^C_C - G^{CD}Q_{DC}. \quad (25)$$

To calculate this for a defect problem would require solution of the full Green matrix and therefore defeat the whole object of the method, so the corrective matrix is approximated by that for the perfect crystal. In other words it is assumed that the CD block of the Green matrix is unchanged between the pure and defective crystals:

$$G^{CD} \approx G^{0CD}. \quad (26)$$

However, since one now has to use a multiplicative correction that is fixed, and in particular whose zeros remain at the same energy, it is clear that the zeros of the defective cluster Q matrix remain poles of the cluster Green matrix and therefore this form of embedding cannot shift the eigenvalues of the problem from those of the isolated cluster.

3.2. The multiplicative corrective operator in a 'skin region'

Suppose the C region is subdivided into the A region, where elements of the Q matrix with the D region may be neglected, and the B region, where they may not, i.e.

$$Q_{AD}^0 = Q_{AD} = 0 \quad Q_{BD}^0 = Q_{BD} \neq 0. \quad (27)$$

The arrangement of the regions A to D in a typical cluster calculation is shown schematically in figure 1. Note that in the language of § 2, the embedding potential is zero in the A region.

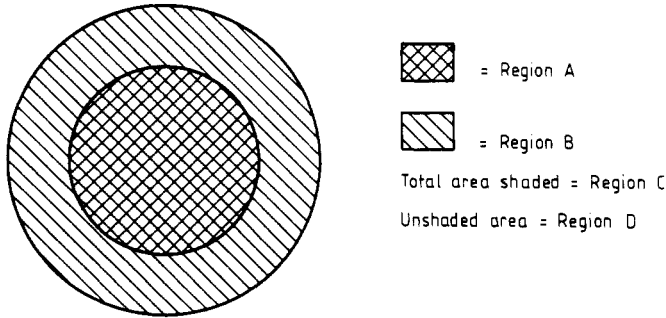


Figure 1. Schematic illustration of regions A, B, C and D for a typical point defect.

This method (Pisani *et al* 1983) aims to recover the exact solution to the Green matrix in the A region by means of a correction applied to the cluster solution in the B region. If equation (23) is written as

$$\begin{bmatrix} G^{AA} & G^{AB} & G^{AD} \\ G^{BA} & G^{BB} & G^{BD} \\ G^{DA} & G^{DB} & G^{DD} \end{bmatrix} \begin{bmatrix} Q_{AA} & Q_{AB} & 0 \\ Q_{BA} & Q_{BB} & Q_{BD} \\ 0 & Q_{DB} & Q_{DD} \end{bmatrix} = \begin{bmatrix} 1^A_A & 0 & 0 \\ 0 & 1^B_B & 0 \\ 0 & 0 & 1^D_D \end{bmatrix} \quad (28)$$

then the first row, first column gives

$$G^{AA}Q_{AA} + G^{AB}Q_{BA} = 1^A_A. \quad (29)$$

So the Green matrix in the A region may be recovered by the correction

$$G^{AA} = (1^A_A - G^{AB}Q_{BA})(Q_{AA})^{-1} \quad (30)$$

where G^{AB} is found as follows: The matrix R^{CC} is defined as the inverse of the Q matrix Q_{CC} for the entire cluster,

$$R^{CC} = (Q_{CC})^{-1}. \quad (31)$$

Then it follows from (22) that

$$G^{CC} = J^C_C R^{CC} \quad (32)$$

and from (28), taking all terms involving the D region across to the right-hand side,

$$\begin{bmatrix} J^A_A & J^A_B \\ J^B_A & J^B_B \end{bmatrix} = \begin{bmatrix} 1^A_A & -G^{AD}Q_{DB} \\ 0 & 1^B_B - G^{BD}Q_{DB} \end{bmatrix} \quad (33)$$

so

$$G^{BA} = (1^B_B - G^{BD}Q_{DB})R^{BA} \equiv K^B_B R^{BA} \quad (34)$$

and

$$G^{AB} = (G^{BA})^T. \quad (35)$$

In order to calculate the corrective operator K^B_B (which is, as can be seen from (33), just one block of the J matrix discussed above), it is again necessary to assume that it does not alter on passing from the pure to the defective crystal. From (34) this is equivalent to the assumption that the Green matrix block G^{BD} is approximately unchanged:

$$G^{BD} \approx G^{0BD}. \quad (36)$$

Note that in this method it is necessary to solve the problem for the *whole* cluster in order to obtain information only about the A region. The results will again show spurious singularities not only at the eigenvalues of the whole defective cluster, introduced via the use of the R matrix in equation (34), but also at the eigenvalues of the isolated A region. These last are introduced via the use of $(Q_{AA})^{-1}$ in equation (30).

3.3. The additive correction to the Green matrix

In this method a correction is added to the inverse of the cluster Q matrix to recover an approximation to the Green matrix within the cluster (Pisani 1987). Again starting from equation (23), the expression

$$G^{CC} = (Q_{CC})^{-1} + (Q_{CC})^{-1}Q_{CD}G^{DD}Q_{DC}(Q_{CC})^{-1} \quad (37)$$

for the cluster Green matrix can be obtained. The approximation is then made, in order to be able to calculate this correction, that the Green matrix *outside* the cluster in the DD block is not altered on passing from the pure to the defective crystal.

However, such an additive approximation for the Green matrix itself has severe

disadvantages. In particular, for any given cluster Q matrix, the exact correction must subtract off the poles that occur in the inverse of the cluster Q matrix at the eigenvalues of the isolated cluster and add on other poles at the eigenvalues of the defective crystal. Any approximation to the correction will remove the exact cancellation of the cluster poles and lead to spurious features in the solution. This is clearly illustrated in the examples given below in § 4.

3.4. General comments

The approximation schemes described in this section do have one attractive feature, namely that the assumptions they make regarding the constancy of various parts of the Green matrix are consistent with those that one would like to make concerning the density matrix. It would be useful to assume, for example, consistently with the method described in §3.3, that the density matrix in the D region is left unaltered at its perfect-crystal value. However, the constancy of the Green matrix at each energy is a much stronger assumption than the constancy of the density matrix (which is related to the integral of the Green matrix with respect to energy), and it seems that it is not justified in view of the errors it introduces into the solution.

It should be noted that these schemes *also* make the fundamental assumption used in the embedding potential method that the Q matrix remains constant outside the CC block, or, put another way, that a finite orbital subset C can be found such that equation (10) is satisfied to some required accuracy. This inevitably involves some approximation since, although the atomic orbitals will usually be exponentially localised, the self-consistent solution for the charge density will generate multipole potentials which decay only as an inverse power of distance if there is no screening by free carriers.

4. Simple examples

We now illustrate how the formal schemes described above yield differing solutions to certain simple model problems. Although it is not a good model of any physical situation (see Stoneham 1975 and references therein), the one-band, one-site model for a defect, where the perturbation representing the defect is confined to a single element in the basis of Wannier functions, has the virtue of being simply soluble and provides a convenient illustration.

4.1. The one-band, one-site model in one dimension

For simplicity we consider first the one-dimensional case where, if the 'site energy' for the perfect chain is E_0 and the hopping matrix element is $-\beta$, then the diagonal element of the perfect-chain Green matrix in the site representation is

$$G^{CC}(E) = \begin{cases} [(E - E_0)^2 - 4\beta^2]^{-1/2} & E - E_0 > 2\beta \\ -i[4\beta^2 - (E - E_0)^2]^{-1/2} & |E - E_0| < 2\beta \\ -[(E - E_0)^2 - 4\beta^2]^{-1/2} & E - E_0 < -2\beta. \end{cases} \quad (38)$$

Take the 'cluster' to consist just of the single orbital at the defect site; then the embedding

potential is

$$\Sigma_{CC}(E) = \begin{cases} (E - E_0) - [(E - E_0)^2 - 4\beta^2]^{1/2} & E - E_0 > 2\beta \\ (E - E_0) - i[4\beta^2 - (E - E_0)^2]^{1/2} & |E - E_0| < 2\beta \\ (E - E_0) + [(E - E_0)^2 - 4\beta^2]^{1/2} & E - E_0 < -2\beta. \end{cases} \quad (39)$$

From this one can solve for the energies of localised states below or above the band

$$E = \begin{cases} E_0 + [(E_0 - E_1)^2 + 4\beta^2]^{1/2} & E_1 > E_0 \\ E_0 - [(E_0 - E_1)^2 + 4\beta^2]^{1/2} & E_1 < E_0 \end{cases} \quad (40)$$

and also find the local density of states at the perturbed site:

$$\rho^{CC}(E) = \frac{[4\beta^2 - (E - E_0)^2]^{1/2}}{\pi[(E_1 - E_0)^2 - (E - E_0)^2 + 4\beta^2]}. \quad (41)$$

These results are identical to those obtained using the Dyson equation directly (Stoneham 1975).

Using the approximation described in § 3.1 above gives the corrective operator J for the perfect crystal as

$$J^C_C(E) = \begin{cases} (E - E_0)[(E - E_0)^2 - 4\beta^2]^{-1/2} & E > E_0 + 2\beta \\ -i(E - E_0)[4\beta^2 - (E - E_0)^2]^{-1/2} & |E - E_0| < 2\beta \\ -(E - E_0)[(E - E_0)^2 - 4\beta^2]^{-1/2} & E < E_0 - 2\beta. \end{cases} \quad (42)$$

This does not produce a state outside the band for $|E_1 - E_0| < 2\beta$, and predicts the local density of states at the defect site for energies within the band to be

$$\rho^{CC}(E) = (1/\pi)(E - E_0)(E - E_1)^{-1}[4\beta^2 - (E - E_0)^2]^{-1/2}. \quad (43)$$

Note the spurious feature at $E = E_1$ and the zero at $E = E_0$.

The method of § 3.2 is not applicable in this case, since there is no B region.

The method of § 3.3 yields a correction

$$\Delta^{CC}(E) = \begin{cases} [(E - E_0)/(E - E_1)]^{-2} \\ \quad \times \{[(E - E_0)^2 - 4\beta^2]^{-1/2} - (E - E_0)^{-1}\} & |E - E_0| > 2\beta \\ [(E - E_0)/(E - E_1)]^2 \\ \quad \times \{-i[4\beta^2 - (E - E_0)^2]^{-1/2} - (E - E_0)^{-1}\} & |E - E_0| < 2\beta \end{cases} \quad (44)$$

to the cluster Green matrix. Again this fails to remove the singularity at $E = E_1$, and gives a density of states within the band ($E \neq E_1$)

$$\rho^{CC}(E) = (1/\pi)(E - E_0)^2(E - E_1)^{-2}[4\beta^2 - (E - E_0)^2]^{-1/2} \quad (45)$$

with the same faults as (43).

4.2. The one-band, one-site model in three dimensions

A similar model calculation has been performed for a one-band, one-site problem in a three-dimensional simple cubic lattice using as a cluster the defective atom and its six nearest neighbours. The central, defective, site constitutes the A region for this cluster

and its neighbours the B region. Analytical results are not available in the energy domain for this case, but the solutions for the local density of states on the whole cluster and at the defect site obtained numerically by the Dyson-equation (or embedding-potential) method and by the approximation schemes in §§ 3.1–3.3 above are shown in figure 2, except that only the result for the defect site is shown for the approximation in § 3.2. The Hamiltonian element at the impurity site is $E_1 = E_0 - 2\beta$. Results are also shown (in figure 3) for the 'smeared' local density of states obtained from the Green function

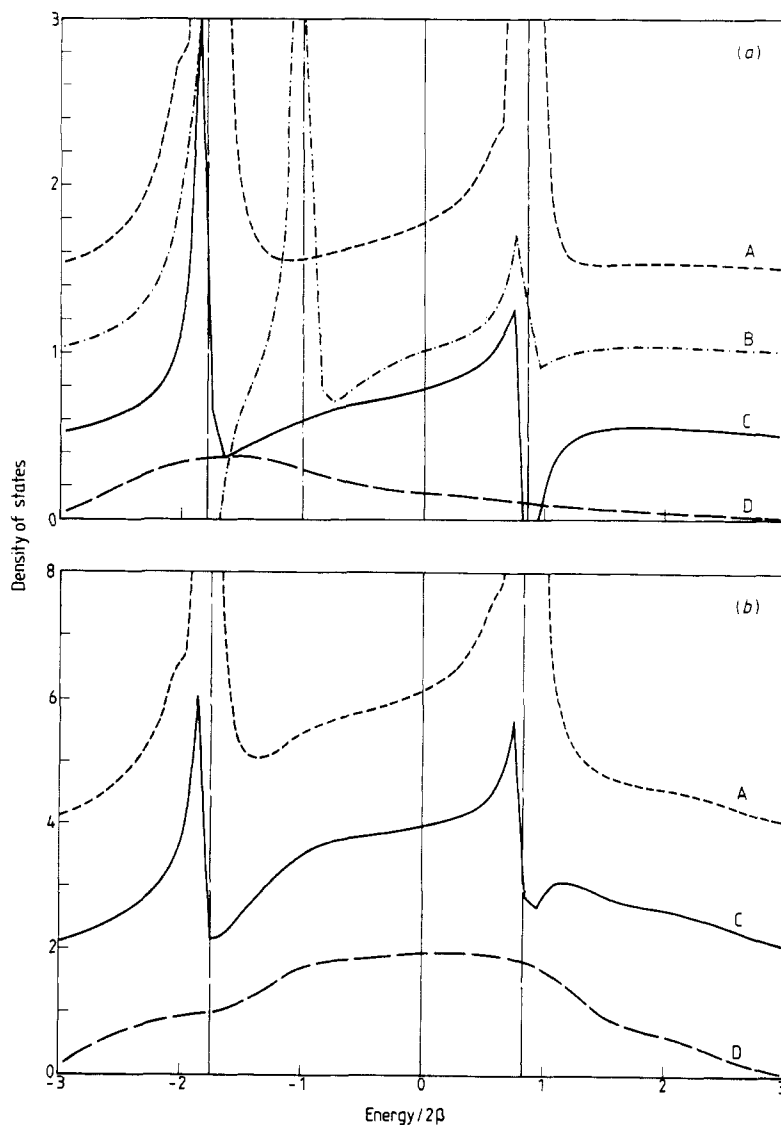


Figure 2. Results for the local density of states on (a) the central atom and (b) the whole cluster obtained from the Dyson-equation (or the embedding-potential) method and the approximation schemes as follows: A, additive corrective; B, multiplicative corrective (skin region); C, multiplicative corrective (whole cluster); D, full embedding of cluster (Dyson equation); E, no embedding of cluster. All energies are in units of 2β . —, position of eigenvalues of isolated cluster; — · —, position of eigenvalue of isolated A region.

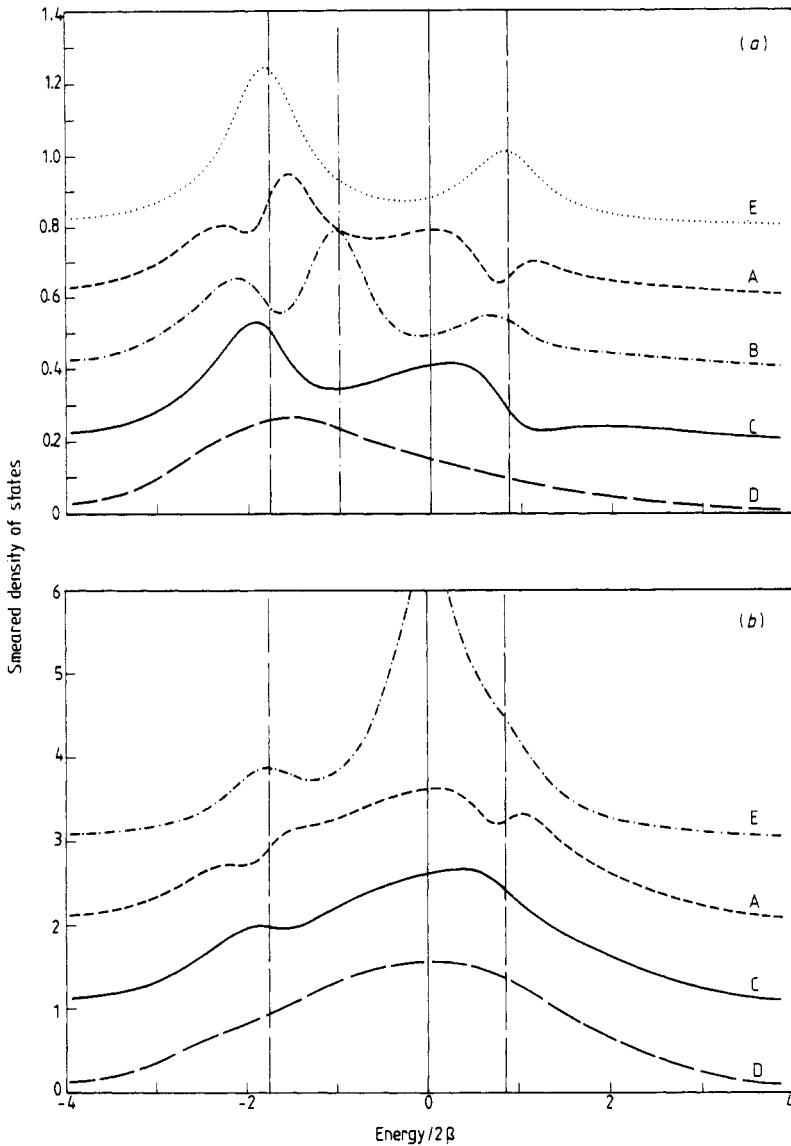


Figure 3. Results for the smeared local density of states on (a) the central atom and (b) the whole cluster obtained from the Dyson-equation (or the embedding-potential) method and the approximation schemes as in figure 2. All energies are in units of 2β and the imaginary component added to the energy in the smearing process is β . The vertical lines are as in figure 2.

when it is analytically continued into the complex plane. In this case the results are compared also with those obtained using just the cluster of six atoms without any embedding corrections at all. The smearing procedure does remove the worst singularities produced by the approximation schemes in §§ 3.1–3.3 and by the non-embedded cluster calculation, but it may be seen that the features in these spectra are nonetheless substantially shifted relative to the exact (Dyson-equation or embedding-potential) result.

5. Matrix elements of operators and normalisation

It is convenient to distinguish two special types of operator:

(i) *Localised* operators which are significant only at or near the defect site and therefore have non-zero matrix elements only in the CC block. In this case one can easily use solutions found for states in the cluster region to obtain matrix elements for the operator taken over the whole space, subject to the normalisation condition on the cluster state function discussed below. The hyperfine interaction with a nuclear spin at the defect site is an example of this type of operator.

(ii) Operators which, while not *localised* at the defect site, are nevertheless *local* in the sense that their matrix elements connect only states nearby in space. Let us assume that an operator \hat{O} is sufficiently local that any changes in the basis set in the cluster region near the defect between the perfect and defective crystals produce changes in the matrix elements of \hat{O} that are confined to the CC block. Suppose the matrix element between two eigenstates ψ_1 and ψ_2 of the full Hamiltonian with eigenvalues E_1 and E_2 is required; this can be broken down into a block matrix equation as follows:

$$\langle \psi_1 | \hat{O} | \psi_2 \rangle = (\psi_1^C)^T O_{CC} \psi_2^C + (\psi_1^C)^T O_{CD} \psi_2^D + (\psi_1^D)^T O_{DC} \psi_2^C + (\psi_1^D)^T O_{DD} \psi_2^D. \quad (46)$$

Using equation (17) ψ_1^D and ψ_2^D can be eliminated to yield

$$\begin{aligned} \langle \psi_1 | \hat{O} | \psi_2 \rangle &= (\psi_1^C)^T O_{CC} \psi_2^C - (\psi_1^C)^T O_{CD} [Q_{DD}(E_2)]^{-1} Q_{DC}(E_2) \psi_2^C \\ &\quad - (\psi_1^C)^T Q_{CD}(E_1) [Q_{DD}(E_1)]^{-1} O_{DC} \psi_2^C \\ &\quad + (\psi_1^C)^T Q_{CD}(E_1) [Q_{DD}(E_1)]^{-1} O_{DD} [Q_{DD}(E_2)]^{-1} Q_{DC}(E_2) \psi_2^C \end{aligned} \quad (47)$$

$$= (\psi_1^C)^T (O_{CC} + \Delta O_{CC}) \psi_2^C \quad (48)$$

where the correction to the operator matrix in the CC block is given by

$$\begin{aligned} \Delta O_{CC} &= -O_{CD} [Q_{DD}(E_2)]^{-1} Q_{DC}(E_2) - Q_{CD}(E_1) [Q_{DD}(E_1)]^{-1} O_{DC} \\ &\quad + Q_{CD}(E_1) [Q_{DD}(E_1)]^{-1} O_{DD} [Q_{DD}(E_2)]^{-1} Q_{DC}(E_2). \end{aligned} \quad (49)$$

This correction is independent of Q_{CC} and O_{CC} and therefore under the conditions outlined above it does not change on passing from the perfect to the defective crystal. Note, however, that it depends on two energies, and this will make it much more difficult to calculate and store; in addition it will not be possible to calculate it in the perfect crystal for use in the defective crystal if there are no perfect-crystal states at one of the required energies E_1 or E_2 .

The localised operators of case (i) above are therefore considerably easier to treat by cluster methods. They may of course be regarded as a special case of (ii) in which the correction happens to be identically zero. In either case it is important that the state functions should be correctly normalised to unity over the whole space $C + D$. This may be achieved using a method due to Inglesfield (1981a): the Green matrix within the cluster, evaluated at some energy E , can be expanded in terms of the eigenfunctions $\Phi_i^C(E)$ of the embedded cluster Hamiltonian at that energy E (normalised to unity over the cluster subspace) and corresponding eigenvalues $E_i(E)$ in the following manner:

$$G^{CC}(E) = (ES_{CC} - H_{CC} - \Sigma_{CC})^{-1} = \sum_i \frac{\Phi_i^C(E) [\Phi_i^C(E)]^T}{E - E_i(E)}. \quad (50)$$

There will be a physical eigenvalue of the system whenever $E_i(E) = E$ for some i . Then the residue of the Green matrix at the resulting pole will be

$$R = [1 - \partial E_i(E)/\partial E]^{-1}|_{E_i=E}. \quad (51)$$

To evaluate R a convenient expression for $\partial E_i/\partial E$ is required. This can be found by pre-multiplying the eigenvalue condition

$$[E_i(E)S_{CC} - H_{CC} - \Sigma_{CC}(E)]\Phi_i^C(E) = 0 \quad (52)$$

by $[\Phi_i^C(E)]^T$, differentiating with respect to E and using the normalisation condition

$$[\Phi_i^C(E)]^T S_{CC} \Phi_i^C(E) = 1 \quad (53)$$

to obtain the result

$$\partial E_i(E)/\partial E = [\Phi_i^C(E)]^T [\partial \Sigma_{CC}(E)/\partial E] \Phi_i^C(E). \quad (54)$$

However, since the imaginary part of the Green matrix is the local density of states, the residue of the cluster part of the Green matrix at an eigenvalue is precisely the fraction of the electron density corresponding to that eigenvalue which lies within the cluster and therefore enables determination of the correct normalisation.

6. The Inglesfield embedding method

Inglesfield (1981a, b) has proposed a method of performing embedding calculations in real space. Let region I be the region in which the Schrödinger equation is to be solved and region II be the rest of space, separated from region I by a surface S . Then if G_{0E} is a Green function satisfying (in units where $m_e = \hbar = 1$)

$$[-\frac{1}{2}\nabla_r^2 + V(r) - E]G_{0E}(\mathbf{r}, \mathbf{r}') = -\delta^3(\mathbf{r} - \mathbf{r}') \quad \mathbf{r}, \mathbf{r}' \text{ in II} \quad (55)$$

he defines an embedding potential Σ_E by

$$\Sigma_E(\mathbf{r}, \mathbf{r}') = G_{0E}^{-1}(\mathbf{r}, \mathbf{r}') + \frac{1}{2} \int_S d^2 \mathbf{r}_s G_{0E}^{-1}(\mathbf{r}, \mathbf{r}_s) (\partial/\partial n_s) G_{0E}(\mathbf{r}_s, \mathbf{r}') \quad \mathbf{r}, \mathbf{r}' \text{ on } S \quad (56)$$

where G_{0E}^{-1} is the inverse of G_{0E} calculated over the surface S :

$$\int_S d^2 \mathbf{r}_s G_{0E}^{-1}(\mathbf{r}, \mathbf{r}_s) G_{0E}(\mathbf{r}_s, \mathbf{r}') = \delta^2(\mathbf{r} - \mathbf{r}') \quad \mathbf{r}, \mathbf{r}' \text{ on } S \quad (57)$$

and $\partial/\partial n_s$ represents the normal derivative at S in the direction outwards from region I into region II. Note that Σ does not depend explicitly on the Hamiltonian throughout region I, but only on the properties of G_{0E} at the surface.

This embedding potential has the properties that the normal derivative at the surface S of any function ψ satisfying the Schrödinger equation in region II with eigenvalue E is given in terms of the values of ψ on S by the integral

$$\partial \psi / \partial n_s(\mathbf{r}_s) = 2 \int_S d^2 \mathbf{r}'_s \Sigma_E(\mathbf{r}_s, \mathbf{r}'_s) \psi(\mathbf{r}'_s) \quad \mathbf{r}_s \text{ on } S. \quad (58)$$

This may also be regarded as a boundary condition to be obeyed on S by solutions of the Schrödinger equation in the full space $I + II$ to ensure that the values and normal derivatives of the wavefunction are continuous at the surface. Such a constraint can

be incorporated automatically by including the embedding potential and a normal derivative term in the Schrödinger equation for region I alone, which becomes

$$\begin{aligned} & \left[-\frac{1}{2}\nabla_r^2 + \frac{1}{2}\delta(n - n_s)\partial/\partial n_s + V(r) \right] \psi(r) - \delta(n - n_s) \int_S d^2r_s \Sigma_E(r, r_s) \psi(r_s) \\ & = E\psi(r) \quad r \text{ in I or on S.} \end{aligned} \quad (59)$$

The advantage of this method is that the inverse of the Green function G_0 is required only on the surface S and not throughout region I as is the case for methods derived directly from the Dyson equation. However, it suffers from the disadvantage that it requires the normal derivative of G_0 at the surface S and this is difficult to obtain accurately. Furthermore, in order to apply the method to a problem stated in terms of a finite basis set, it is necessary first to find the Green function in matrix form, then convert it to spatial form, find its normal derivative, re-expand it in some set of surface functions to find its surface inverse and only then finally to calculate the embedding potential in real space and express it in the desired matrix form.

In the following section an analogous method is presented which enables all the necessary calculations to be performed as matrix manipulations in a single basis and which removes the necessity of evaluating the normal derivative of the Green function. It retains the advantage of requiring the inverse of the host Green function only in a surface region.

7. A modification of the Inglesfield method

If the C region is divided into regions A and B, defined as in § 3.2 above, then equation (7) takes the block matrix form

$$\begin{bmatrix} Q_{AA} & Q_{AB} \\ Q_{BA} & Q_{BA}Q_{BB} - Q_{BD}(Q_{DD})^{-1}Q_{DB} \end{bmatrix} \begin{bmatrix} \psi^A \\ \psi^B \end{bmatrix} = 0. \quad (60)$$

Now if we were to solve for the Green matrix in region B only, it would be subject to Löwdin embedding corrections from the D region and the A region:

$$(G^{BB})^{-1} = Q_{BB} - Q_{BA}(Q_{AA})^{-1}Q_{AB} - Q_{BD}(Q_{DD})^{-1}Q_{DB}. \quad (61)$$

Therefore (60) becomes

$$\begin{bmatrix} Q_{AA} & Q_{AB} \\ Q_{BA} & (G^{BB})^{-1} + Q_{BA}(Q_{AA})^{-1}Q_{AB} \end{bmatrix} \begin{bmatrix} \psi^A \\ \psi^B \end{bmatrix} = 0. \quad (62)$$

If we now note that

$$\begin{bmatrix} G^{AA} & G^{AB} & G^{AD} \\ G^{BA} & G^{BB} & G^{BD} \\ G^{DA} & G^{DB} & G^{DD} \end{bmatrix} \begin{bmatrix} Q_{AA} & Q_{AB} & 0 \\ Q_{BA} & Q_{BB} & Q_{BD} \\ 0 & Q_{DB} & Q_{DD} \end{bmatrix} = \begin{bmatrix} 1^A_A & 0 & 0 \\ 0 & 1^B_B & 0 \\ 0 & 0 & 1^D_D \end{bmatrix} \quad (63)$$

so

$$G^{BA}Q_{AA} + G^{BB}Q_{BA} = 0 \quad (64)$$

implying

$$Q_{BA} = -(G^{BB})^{-1} G^{BA} Q_{AA}. \quad (65)$$

Then substitution in (62) yields the result

$$\begin{bmatrix} Q_{AA} & Q_{AB} \\ Q_{BA} & (G^{BB})^{-1}(1^B_B - G^{BA}Q_{AB}) \end{bmatrix} \begin{bmatrix} \psi^A \\ \psi^B \end{bmatrix} = 0. \quad (66)$$

The analogue of the Inglesfield boundary condition (58) is now the equation given by the second row of the above, namely

$$Q_{BA}\psi^A + (G^{BB})^{-1}(1^B_B - G^{BA}Q_{AB})\psi^B = 0. \quad (67)$$

There is a clear similarity between the form of this expression and equations (56) and (58). Note how the surface derivative of the Green function no longer appears and has been replaced by the Q matrix elements connecting the A and B regions. The inverse of the Green matrix is required only in the B region on the surface of the cluster.

It is clear from this treatment that the real-space and matrix operators labelled Σ by Baraff and Schlüter (1986) are not in fact precisely analogous. It is more exact to say that the equivalent of the real-space embedding potential $\Sigma(r, r')$ in the matrix picture is the whole effective Hamiltonian in the B region. Despite this, the notation of Baraff and Schlüter is retained in this paper for consistency. The distinction is not important in practical applications since the physical Hamiltonian (as opposed to the embedding potential) in real space has zero weight on the surface S.

8. A simple example of a free surface: the truncated tight-binding solid

The Inglesfield method is particularly useful for surface problems where the region I (or the 'C' subset of basis functions) represents the semi-infinite portion which has been removed from the solid and inversion of a Green function over the whole of this region is therefore impossible. Here we consider the simplest possible model of a surface produced by cleaving a simple cubic array of s-like tight-binding orbitals in the (001) plane. Of course, this is not a good model of any real system and, since it may be reduced by translational symmetry parallel to the surface to the problem of a semi-infinite linear chain, it is soluble by other methods, but it does serve to illustrate how calculations on slabs of finite thickness converge to the result given by the modified Inglesfield method as the slab thickness becomes large.

If the diagonal element of the Hamiltonian at each site is E_0 and the hopping integral between nearest neighbours is $-\beta$ then the band structure is

$$E(\mathbf{k}) = E_0 - 2\beta(\cos k_x + \cos k_y + \cos k_z) \quad (68)$$

where k is measured in units (lattice constant)⁻¹.

It is convenient to work in reciprocal space parallel to the surface since the periodicity in this direction still guarantees that the Bloch representation diagonalises the Hamiltonian. If p and q label layers in the z direction and k_x and k_y are wavevectors in the xy plane then the quantity of interest is

$$G_E(p - q, k_x, k_y) = \int_{-\pi}^{\pi} \frac{dk_z \exp[ik_z(p - q)]}{2\pi(E - E(\mathbf{k}))}. \quad (69)$$

Writing

$$\varepsilon = E - E_0 + 2\beta(\cos k_x + \cos k_y) \quad (70)$$

we obtain for $p - q = 0$

$$G_E(0, k_x, k_y) = \begin{cases} (\varepsilon^2 - 4\beta^2)^{-1/2} & \varepsilon > 2\beta \\ -i(4\beta^2 - \varepsilon^2)^{-1/2} & -2\beta < \varepsilon < 2\beta \\ -(\varepsilon^2 - 4\beta^2)^{-1/2} & \varepsilon < -2\beta \end{cases} \quad (71)$$

and for $p - q = 1$

$$G_E(1, k_x, k_y) = \begin{cases} [1 - \varepsilon(\varepsilon^2 - 4\beta^2)^{-1/2}]/2\beta & \varepsilon > 2\beta \\ [1 + i\varepsilon(4\beta^2 - \varepsilon^2)^{-1/2}]/2\beta & -2\beta < \varepsilon < 2\beta \\ [1 + \varepsilon(\varepsilon^2 - 4\beta^2)^{-1/2}]/2\beta & \varepsilon < -2\beta. \end{cases} \quad (72)$$

The 'effective Q operator' in an embedding region which is a layer of atoms parallel to the surface is therefore, using (66),

$$\begin{aligned} (G^{BB})^{-1}(1_B^B - G^{BA}Q_{AB}) &= [1 - \beta G_E(1, k_x, k_y)]/G_E(0, k_x, k_y) \\ &= \begin{cases} [\varepsilon + (\varepsilon^2 - 4\beta^2)^{1/2}]/2 & \varepsilon > 2\beta \\ [\varepsilon + i(4\beta^2 - \varepsilon^2)^{1/2}]/2 & -2\beta < \varepsilon < 2\beta \\ [\varepsilon - (\varepsilon^2 - 4\beta^2)^{1/2}]/2 & \varepsilon < -2\beta. \end{cases} \end{aligned} \quad (73)$$

For this simple problem we can just use the surface layer of atoms as the 'cluster region'

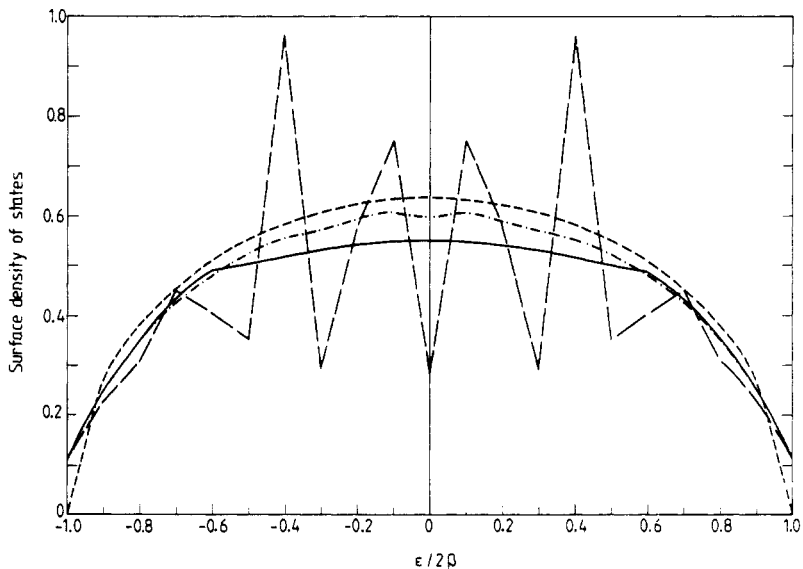


Figure 4. Comparison of densities of states in the surface layer obtained from calculations on slabs of varying widths (—, 10 atoms; ---, 30 atoms; - - -, 50 atoms) and from the exact solution (74) (- · - ·) for the truncated tight-binding model. All energies are in units of 2β .

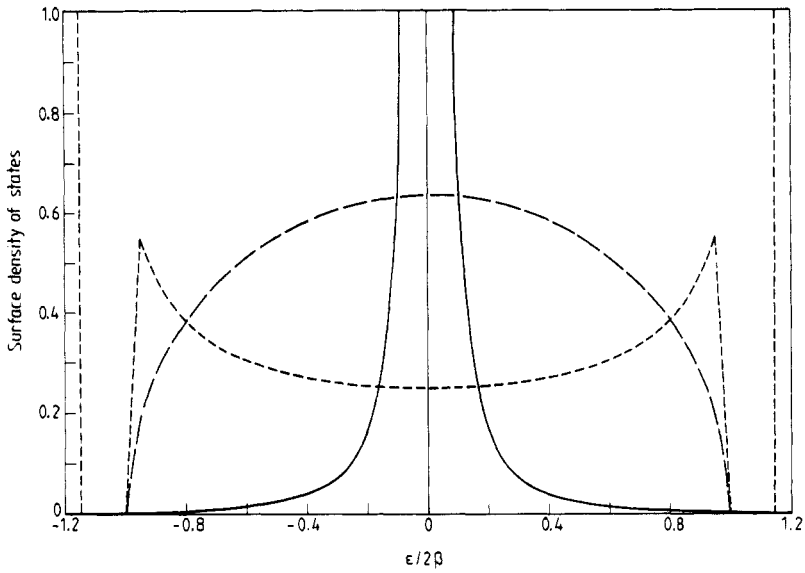


Figure 5. Dependence of the density of states from the exact solution for the truncated tight-binding model on the coupling matrix element γ (—, $\gamma = 0.2\beta$; — —, $\gamma = \beta$; - · - ·, $\gamma = 1.8\beta$) between the surface layer and the bulk. All energies are in units of 2β .

and can find for example the density of states for a given k_x and k_y in the surface layer:

$$\rho(k_x, k_y) = -\text{Im}[Q_{\text{eff}}^{-1}]/\pi = \begin{cases} (1 - \varepsilon^2/4\beta^2)/\pi\beta & -2\beta < \varepsilon < 2\beta \\ 0 & \text{otherwise.} \end{cases} \quad (74)$$

A comparison of this result with those obtained from calculations on slabs of thickness 10, 30 and 50 atoms is shown in figure 4.

If relaxation of the surface atoms is allowed normal to the surface so that the hopping integrals into the subsurface layer are $-\gamma$ rather than $-\beta$, then the embedding potential must be applied in the subsurface layer and a matrix problem solved in the two outermost layers. Assuming the hopping matrix elements are left unaltered parallel to the surface, the elements of the Green function are

$$\begin{bmatrix} \varepsilon & \gamma \\ \gamma & Q_{\text{eff}}(\varepsilon) \end{bmatrix}^{-1} = \frac{1}{\varepsilon Q_{\text{eff}}(\varepsilon) - \gamma^2} \begin{bmatrix} Q_{\text{eff}}(\varepsilon) & -\gamma \\ -\gamma & \varepsilon \end{bmatrix}. \quad (75)$$

The resulting density of states in the surface layer as a function of ε is shown in figure 5. Note how in the limit $\gamma \rightarrow 0$ the surface layer becomes decoupled from the bulk and the energy of the state is entirely determined by k_x and k_y so the density of states tends to a delta function at $\varepsilon = 0$, while for $\gamma > (\sqrt{2})\beta$ the surface states actually move outside the bulk band energy and become localised at the surface.

9. Invariance under change of boundary

Given a single-particle Hamiltonian and some basis set and granted the fundamental assumption that the Hamiltonian matrix and overlap matrix differ between the perfect

and defective crystals only in the cluster region, there are no further approximations involved in the methods described. The results must therefore be independent of precisely where the boundary of the cluster is drawn provided only that it is consistent with the above fundamental assumption. Transfer of some number of orbitals from the D set to the C set (in the matrix method) or movement of the surface S to incorporate some of region II into region I (in the real-space method), together with appropriate modifications of the embedding potential, must yield the same answer for the Green function in the defect or surface region. This enables us to derive implicit expressions for the embedding potential in both the matrix and real-space representations that do not involve the perfect-crystal Green function.

In the matrix formalism we can express this invariance under boundary motion by the statement that if the Green matrix for some cluster region R is correctly generated by an embedding potential Σ_R then

$$G^{RR} = (Q_{RR} - \Sigma_R)^{-1} \quad (76)$$

and if an additional orbital set S is then added to R to form the set T, then the RR block of the new Green matrix must be the same as the old G^{RR} . If the set S is chosen so that it includes all the orbitals in T for which the new embedding potential is non-zero, we obtain the matrix relation

$$\begin{bmatrix} G^{RR} & G^{RS} \\ G^{SR} & G^{SS} \end{bmatrix} \begin{bmatrix} Q_{RR} & Q_{RS} \\ Q_{SR} & Q_{SS} - \Sigma_S \end{bmatrix} = \begin{bmatrix} 1^R_R & 0 \\ 0 & 1^S_S \end{bmatrix}. \quad (77)$$

The first row of this written out is

$$G^{RR}Q_{RR} + G^{RS}Q_{SR} = 1^R_R \quad (78a)$$

$$G^{RR}Q_{RS} + G^{RS}(Q_{SS} - \Sigma_S) = 0 \quad (78b)$$

Eliminating G^{RS} and using (76) we obtain

$$\Sigma_R = Q_{RS}(Q_{SS} - \Sigma_S)^{-1}Q_{SR}. \quad (79)$$

As it stands this expression is not particularly useful since it relates the embedding corrections appropriate to successive shells which stretch away to infinity, although it is interesting to note that the expression is analogous to those obtained in the recursion method (Haydock 1980) where a basis set is explicitly constructed so that a single orbital has the properties of the S region above. If, however, the R and S regions are related by a symmetry operation of the perfect lattice then the two embedding potentials are the same:

$$\Sigma_R = \Sigma_S = \Sigma \quad (80)$$

and therefore (29) becomes

$$\Sigma = Q_{RS}(Q_{SS} - \Sigma)^{-1}Q_{SR} \quad (81)$$

which is an implicit equation for Σ which does not involve the solution of any Green function. It can only be solved explicitly if the Q and Σ matrices commute, i.e. if the R and S regions each contain only one orbital or one set of orbitals on which the Hamiltonian can be immediately block-diagonalised. The one-band tight-binding solid with nearest-neighbour hopping described above is such a case and here the solution of (81) immediately yields the result (73).

Even in cases when it cannot be solved explicitly, (81) yields a very simple iterative

method for finding Σ which resembles a recursion series in which the coefficients at each step are the same.

The most obvious type of problem for which successive embedding regions are likely to be related by lattice symmetry operations is the embedding of a surface, where the symmetry is a lattice translation. To derive the result in the Inglesfield real-space picture corresponding to (81) we therefore consider a surface S lying in a plane $z = A$ where A is some constant. Since the Green function $G_E(\mathbf{r}, \mathbf{r}')$ with \mathbf{r}' in region I satisfies the Schrödinger equation with eigenvalue E for \mathbf{r} in region II it also satisfies the Inglesfield boundary condition on S :

$$(\partial/\partial z)G_E(\mathbf{r}, \mathbf{r}') = 2 \int_S d^2\mathbf{r}_s \Sigma_E(\mathbf{r}, \mathbf{r}_s) G_E(\mathbf{r}_s, \mathbf{r}') \quad \mathbf{r} \text{ on } S, \mathbf{r}' \text{ in I.} \quad (82)$$

Differentiating both sides with respect to z we obtain

$$(\partial^2/\partial z^2)G_E(\mathbf{r}, \mathbf{r}') = 2 \int_S d^2\mathbf{r}_s \{ \Sigma_E(\mathbf{r}, \mathbf{r}_s) (\partial/\partial z_s) G_E(\mathbf{r}_s, \mathbf{r}') + [(\partial/\partial z) \Sigma_E(\mathbf{r}, \mathbf{r}_s)] G_E(\mathbf{r}_s, \mathbf{r}') \} \quad \mathbf{r} \text{ on } S, \mathbf{r}' \text{ in I} \quad (83)$$

and substituting on the right-hand side from (82) gives

$$(\partial^2/\partial z^2)G_E(\mathbf{r}, \mathbf{r}') = 2 \int_S d^2\mathbf{r}_s [(\partial/\partial z) \Sigma_E(\mathbf{r}, \mathbf{r}_s)] G_E(\mathbf{r}_s, \mathbf{r}') + 4 \int_S d^2\mathbf{r}_s \int_S d^2\mathbf{r}'_s \Sigma_E(\mathbf{r}, \mathbf{r}_s) \Sigma_E(\mathbf{r}_s, \mathbf{r}'_s) G_E(\mathbf{r}'_s, \mathbf{r}') \quad \mathbf{r} \text{ on } S, \mathbf{r}' \text{ in I.} \quad (84)$$

However

$$(\partial^2/\partial z^2)G_E(\mathbf{r}, \mathbf{r}') = \{2[V(\mathbf{r}) - E] - (\partial^2/\partial x^2) - (\partial^2/\partial y^2)\} G_E(\mathbf{r}, \mathbf{r}') \quad \mathbf{r} \text{ on } S, \mathbf{r}' \text{ in I.} \quad (85)$$

So, pre-multiplying both sides of (84) by the surface inverse of Σ , which satisfies

$$\int_S d^2\mathbf{r}_s \Sigma_E^{-1}(\mathbf{r}, \mathbf{r}_s) \Sigma_E(\mathbf{r}_s, \mathbf{r}') = \delta^2(\mathbf{r} - \mathbf{r}') \quad \mathbf{r}, \mathbf{r}' \text{ on } S \quad (86)$$

and integrating over the surface S we obtain

$$\begin{aligned} & \int_S d^2\mathbf{r}_s \Sigma_E^{-1}(\mathbf{r}, \mathbf{r}_s) \{2[V(\mathbf{r}_s) - E] - (\partial^2/\partial x_s^2) - (\partial^2/\partial y_s^2)\} G_E(\mathbf{r}_s, \mathbf{r}') \\ &= 2 \int_S d^2\mathbf{r}_s \int_S d^2\mathbf{r}'_s \Sigma_E^{-1}(\mathbf{r}, \mathbf{r}_s) [(\partial/\partial z_s) \Sigma_E(\mathbf{r}_s, \mathbf{r}'_s)] G_E(\mathbf{r}'_s, \mathbf{r}') \\ &+ 4 \int_S d^2\mathbf{r}_s \Sigma_E(\mathbf{r}, \mathbf{r}_s) G_E(\mathbf{r}_s, \mathbf{r}') \quad \mathbf{r} \text{ on } S, \mathbf{r}' \text{ in I.} \end{aligned} \quad (87)$$

Finally we integrate by parts on the left-hand side, post-multiply by the surface inverse of G_E and integrate once more over S to obtain the result

$$\begin{aligned} & \{2[V(\mathbf{r}) - E] - (\partial^2/\partial x^2) - (\partial^2/\partial y^2)\} \Sigma_E^{-1}(\mathbf{r}, \mathbf{r}') \\ &= 4\Sigma_E(\mathbf{r}, \mathbf{r}') + 2 \int_S d^2\mathbf{r}_s \Sigma_E^{-1}(\mathbf{r}, \mathbf{r}_s) (\partial/\partial z) \Sigma_E(\mathbf{r}_s, \mathbf{r}') \quad \mathbf{r}, \mathbf{r}' \text{ on } S. \end{aligned} \quad (88)$$

So far, no symmetry property of the perfect crystal normal to the surface has been used. There are two important cases:

(i) Perfect translational symmetry in the z direction. In this case

$$(\partial/\partial z)\Sigma_E(x, y, z, x', y', z) = 0 \quad (89)$$

and (88) reduces to

$$\{2[V(\mathbf{r}) - E] - (\partial^2/\partial x^2) - (\partial^2/\partial y^2)\} \Sigma_E^{-1}(\mathbf{r}, \mathbf{r}') = 4 \Sigma_E(\mathbf{r}, \mathbf{r}') \quad \mathbf{r}, \mathbf{r}' \text{ on } S. \quad (90)$$

(ii) Symmetry under translation in the z direction through certain discrete amounts. Suppose the planes $z = A$ and $z = B$ are equivalent under such a translation; then

$$\Sigma_E(x, y, A, x', y', A) = \Sigma_E(x, y, B, x', y', B) \quad (91)$$

so

$$\int_{z=A}^{z=B} dz (\partial/\partial z) \Sigma_E(\mathbf{r}, \mathbf{r}') = 0. \quad (92)$$

Therefore, from (88) we have

$$\begin{aligned} (\partial/\partial z) \Sigma_E(\mathbf{r}, \mathbf{r}') &= \frac{1}{2} \int_S d^2 \mathbf{r}_s \Sigma_E(\mathbf{r}, \mathbf{r}_s) \{2[V(\mathbf{r}_s) - E] - (\partial^2/\partial x_s^2) - (\partial^2/\partial y_s^2)\} \Sigma_E^{-1}(\mathbf{r}_s, \mathbf{r}') \\ &\quad - 2 \int_S d^2 \mathbf{r}_s \Sigma_E(\mathbf{r}, \mathbf{r}_s) \Sigma_E(\mathbf{r}_s, \mathbf{r}') \end{aligned} \quad (93)$$

and applying (92), we obtain

$$\begin{aligned} \int_{z=A}^{z=B} dz \int_S d^2 \mathbf{r}_s \Sigma_E(\mathbf{r}, \mathbf{r}_s) \{2[V(\mathbf{r}_s) - E] - (\partial^2/\partial x_s^2) - (\partial^2/\partial y_s^2)\} \Sigma_E^{-1}(\mathbf{r}_s, \mathbf{r}') \\ = 4 \int_{z=A}^{z=B} dz \int_S d^2 \mathbf{r}_s \Sigma_E(\mathbf{r}, \mathbf{r}_s) \Sigma_E(\mathbf{r}_s, \mathbf{r}'). \end{aligned} \quad (94)$$

Equation (90) is easy to solve when there is also translational symmetry parallel to the surface (i.e. for the case of a free-electron gas). Otherwise it seems that (90) and (94) will not be so convenient for iterative solution as (81) but they are of some interest as a check on any solution that is found from a Green function, especially when doubts exist concerning the accuracy of the normal derivative of the Green function at the surface S .

10. Computational considerations

Suppose there are N elements in the subset C of the basis set and that the size of the problem cannot be reduced by symmetry. Then each matrix inversion or multiplication takes $O(N^3)$ operations, so it is of the utmost importance to reduce the number of such operations involved. The extraction of the defective-crystal Green function by explicit solution of the Dyson equation (as opposed to iterative solution, which requires no inversions but diverges when a bound state is formed) and by inversion of the cluster Q matrix with an embedding correction each require one such inversion, but the Dyson-equation method requires in addition two matrix multiplications.

Turning now to the calculation of the perfect-crystal Green function or embedding potential for use in the defect calculation, the embedding-potential method involves performing an additional inversion once the cluster-projected Green function has been obtained. The time required by the Dyson-equation and embedding-potential methods will therefore be approximately equal for a given problem. If only quantities integrated over the energy E are required, the integration over the Brillouin zone necessary to calculate the perfect-crystal Green function may be eased by distorting the contour for the energy integration away from the real axis into the complex plane (Williams *et al* 1982).

However the perfect-crystal calculation has to be done only once for a given cluster shape and so there are circumstances in which the particular advantages of the embedding-potential method may carry the day. First, if the embedding potential is non-zero over only a very small part of the cluster, then much less space will be required to store the embedding potential than to store the Green function over the whole cluster. The problem of an interface where the 'cluster' region is effectively infinite is an extreme case and is insoluble by the Dyson-equation technique without further approximation.

Secondly, the presence of a bound state will be signalled by the presence of a pole in the Green function, which it may be difficult to locate accurately, particularly if the energy is moved some way off the real axis so that the corresponding delta function in the local density of states is smoothed to a Lorentzian which can be easily integrated numerically in order to find the density matrix. The embedding-potential method, in contrast, enables easy location of the bound state by solution of the embedded Schrödinger equation at real energy and also, via equation (51), of the area under the corresponding delta function in the local density of states.

11. Other problems involving subdomains

It is possible to apply these methods to other problems of electronic structure where the basis subsets are separated not in real space but in some other parameter such as energy. The techniques discussed in § 2 have been used in just this way in the 'peripheral orbital method' (Louie 1980, Lodge 1986) to include implicitly the effects of higher-lying d states in band-structure calculations for predominantly sp-bonded semiconductors (Louie 1980, 1982). Since the separation between the bands of interest is much less than the excitation energy into the d states, it is usually sufficient to neglect the energy dependence of the 'embedding potential' in this case.

There is also a simple isomorphism between single-electron tight-binding calculations and the equations of motion for a collection of atoms subject to harmonic forces (i.e. forces varying quadratically with displacement): the Hamiltonian is replaced by the dynamical matrix D and the single electron energy E by the square of the normal mode frequency ω^2 . The embedding potential becomes the linear response function of the bulk solid to displacements within the cluster region. Green function methods derived from the Dyson equation are well established in problems of this sort, but the Inglesfield method, since it relied in its original form on the solution of a real-space rather than a matrix equation, has not been used in vibrational problems. The discrete basis adaptation of the Inglesfield method described here is, however, suitable for the vibrational case and might be especially useful in calculating phonon modes associated with surfaces or interfaces.

12. Conclusions

A consistent framework exists for the embedding of defect cluster calculations in the independent-electron or harmonic-lattice approximation. The Dyson-equation method is closely related to the Inglesfield method but not to other 'corrective operator' schemes that have been proposed and involve unnecessary additional approximations. Further work is required to extend the above ideas to cases where the Hamiltonian is not quadratic in the field operators (i.e. to problems involving interacting electrons or an anharmonic lattice).

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