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A comparison of techniques for embedding defect cluster calculations*

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Cluster calculations have proved one of the most fruitful means of extracting useful information about solid-state defect properties at finite computational expense, but large clusters are necessary to obtain reliable results and uncertainty always remains concerning the effects of edge states, with "ad hoc" boundary conditions such as the saturation of the surface with hydrogen atoms being frequently employed. Recently methods have been developed for "embedding" the cluster in the perfect crystal so that the solution obtained from the cluster calculation is the same as would have been obtained from a full calculation on the whole defective solid. Here the relationships of these methods with each other and with "perturbed crystal" methods which modify the perfect crystal solution to account for the presence of the defect are explored. It is shown that the "embedding potential" technique is preferable and is equivalent to methods that have been used in other fields.

Key words: Point defect theory — Subdomains of a quantum system — Embedding potential — Cluster calculations in solids

1. Introduction

What equations of motion must be solved within a subdomain of a quantum system to obtain within that subdomain the solution of the full equation of motion

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for the whole system? In the language of the theory of point defects one may use either (see, for example, [1, 2]):

1. The "perturbed crystal" approach where one calculates the effect on the solution for the perfect crystal of a perturbation of finite range representing the defect, or

2. the "perturbed cluster" approach where one calculates the effect of the surrounding medium on the solution for a cluster of atoms surrounding the defect.

The two methods are equivalent and both lead to the concept of an energy-dependent "embedding potential" which must be added to the Hamiltonian within the defect region. Other embedding methods [1, 3, 4] which do not emerge naturally from both approaches involve additional unnecessary approximations.

2. Single particle formalism

Suppose the system of interest may be sufficiently described by a (non-orthogonal) set of basis kets $\{|\phi_\alpha\rangle\}$ so that the problem may be stated in matrix form. For convenience in dealing with a non-orthogonal basis we adopt the notation of Ballentine and Kolar [5] since this enables the matrix relations to be written in a natural and unambiguous way. One defines a dual basis set $\{|\phi^\alpha\rangle\}$ by

$$|\phi^\alpha\rangle = \sum_\beta (S^{-1})^{\beta\alpha} |\phi_\beta\rangle \tag{1}$$

where

$$S_{\alpha\beta} = \langle\phi_\alpha | \phi_\beta\rangle \tag{2}$$

so that

$$\langle\phi^\alpha | \phi_\beta\rangle = \delta^\alpha{}_\beta . \tag{3}$$

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

$$|u\rangle = \sum_\alpha u^\alpha |\phi_\alpha\rangle = \sum_\alpha u_\alpha |\phi^\alpha\rangle \tag{4}$$

and operators may be represented in four different matrix forms. Following Pisani [2] the operator $\hat{Q}$ is defined by

$$\hat{Q}(E) = E\hat{I} - \hat{H} \tag{5}$$

where H is the Hamiltonian and I the identity operator. The Green matrix is defined through

$$\sum_\gamma G^{\alpha\gamma} Q_{\gamma\beta} = \delta^\alpha{}_\beta \tag{6}$$

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

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. This is inevitably an approximation since any defect will generate a multipole field of some order which falls off only as an inverse power of distance unless it is screened.

Then the fundamental equation of "perturbed crystal" theory is the Dyson equation

$$G^{CC} = G^{0CC} + G^{0CC} V_{CC} G^{CC} \tag{7}$$

where the superscript 0 always refers to the perfect crystal and V is (minus) the difference between the Q-matrices in the CC-block between the defective and perfect crystals:

$$V_{CC} = -(Q_{CC} - Q^0_{CC}). \tag{8}$$

Equations (7) and (8) are equivalent to

$$(G^{CC})^{-1} = Q_{CC} - Q^0_{CC} + (G^{0CC})^{-1} \tag{9}$$

which is the "perturbed cluster" equation of Baraff and Schluter [6]. 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"

$$\sum_{CC}(E) = Q^0_{CC} - (G^{0CC})^{-1}. \tag{10}$$

The existence of such an effective potential had also been noted by other authors [7].

One can obtain exactly the same result from the "perturbed cluster" viewpoint. The Schrödinger equation may be written in the block matrix form

$$\begin{bmatrix} Q_{CC} & Q_{CD} \\ Q_{DC} & Q_{DD} \end{bmatrix} \begin{bmatrix} \psi^C \\ \psi^D \end{bmatrix} = 0 \tag{11}$$

and therefore ([8])

$$[Q_{CC} - Q_{CD}(Q_{DD})^{-1} Q_{DC}]\psi^C = 0. \tag{12}$$

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

$$\sum_{CC}(E) = Q_{CD}(Q_{DD})^{-1} Q_{DC}. \tag{13}$$

By assumption all the quantities on the right-hand side are unchanged between the perfect and defective crystals so one can calculate it given the cluster-projected perfect crystal Green matrix for which one can solve by exploiting translational symmetry: this is equivalent to the Baraff-Schluter formula.

In Eq. (13) 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 in perturbed crystal theory [9]. 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.

3. Many-body aspects of the problem

The simplest case of many-body interactions is that in which the bulk solid may be adequately described by a single electron picture, i.e. by a band structure of some kind, but many-body effects are important locally at the defect site. Then one would expect that the above expressions for the effective embedding potential will still hold. This may be demonstrated specifically from both the perturbed cluster and perturbed crystal viewpoints.

4. Corrective operator methods

The other solutions of the embedding problem which have been proposed without reference to the perturbed crystal formalism involve different types of correction. These do not share with the embedding potential the feature of being independent of the CC-block of the Q-matrix, which, like the embedding potential method, they assume is the only part of the Q-matrix to change. Additional assumptions about the Green matrix are necessary in these methods in order to use corrections calculated for the perfect problem to embed the cluster in the defective crystal. Because these methods involve corrections to the Green matrix itself rather than to the Hamiltonian, the approximations used mean that the poles in the Green matrix at the eigenvalues of the isolated cluster are not fully removed. Three methods have been suggested:

1. A multiplicative corrective operator is used [3] to pass from the inverse of the Q-matrix in the cluster region to the Green function within that region. This method assumes that

$$G^{CD} = G^{0CD}. \tag{14}$$

2. The corrective operator is applied in the "skin region" [1] at the outside of the cluster where the Q-matrix elements with the bulk are non-zero, i.e. where the embedding potential is non-zero. If this region is denoted by B, then this method assumes that

$$G^{BD} = G^{0BD}. \tag{15}$$

3. An additive correction is applied to the inverse of the cluster Q-matrix to generate the Green matrix [4]. This method assumes that

$$G^{DD} = G^{0DD}. \tag{16}$$

At first sight it seems that these assumptions are consistent with the requirement that there be no change in space charge (since this would change the potential) outside the cluster. However the constancy of the Green matrix at each energy separately is a much stronger assumption than the constancy of the density matrix.

Simple examples such as the one-band, one-site model which can be solved exactly using the Dyson equation [10] or the embedding potential methods show clearly the undesirable features which the corrective operator techniques introduce near eigenvalues of the isolated cluster.

5. Other applications of the formalism

Note that although here the procedure has been described in terms of the connection of two subdomains which are spatially separated, one could just as well use C and D regions separated in energy. This is precisely what is done in the "Peripheral Orbital" approach [11, 12] which has been used to include indirectly the effects of the d-orbitals in band structure calculations for semiconductors [13]. In this case one may usually assume that the embedding potential is approximately independent of energy.

The fermion Green functions used in these derivations can be replaced by Zubarev Green functions for particle positions and momenta [14]. Then exactly analogous algebra shows that the dynamical behaviour of a cluster of particles, interacting among themselves with arbitrary many-body or anharmonic forces, which interacts harmonically with a harmonic embedding region, is the same as that of the isolated cluster with additional harmonic springs between the particles whose spring constants are frequency dependent. In the classical limit this amounts to the replacement of the harmonic embedding region by its linear response function.

6. Conclusion

The embedding potential method and equivalent techniques are to be preferred to the other methods which have been used to solve the problem of a subdomain of a quantum system, both in the theory of point defects and in other applications

It is hoped to publish a more complete account of this work and its relation to other methods in the theory of defects and surfaces shortly.

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