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## GREEN'S FUNCTION MATCHING METHOD FOR REALISTIC CALCULATIONS OF INTERFACES

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**Résumé** - On propose une nouvelle méthode de calcul de la structure électronique des interfaces, qui n'utilise pas des périodicités artificielles. Les ingrédients fondamentaux de la méthode sont (a) le formalisme de la fonction de Green de surface, développé par Garcia-Moliner et al.; et (b) la méthode de la fonction de Green autoconsistante, appliquée avec succès aux défauts dans les semiconducteurs. Des résultats préliminaires, qui montrent la valeur pratique de la méthode, sont exposés.

**Abstract** - A new method for the calculation of the electronic structure of interfaces is proposed, which avoids the introduction of artificial periodicities. The basic ingredients of the method are (a) the Green's function matching formalism, put forward by Garcia-Moliner et al.; and (b) the self-consistent Green's function approach, as successfully applied to defects in semiconductors. Preliminary results, which indicate the feasibility of the procedure, are presented.

## I - INTRODUCTION

Modern electronic structure calculations, based on the local density functional approximation, have been applied most frequently to finite systems, such as atoms or molecules, or to infinite periodic solids. Their application to non-periodic infinite systems, like solids with defects or surfaces and interfaces, is more problematic. In the case of point defects, the description of the electronic structure in terms of the Green's function formalism based on the Dyson equation provided satisfactory self-consistent solutions for both semiconductors /1,2/ and metals /3/.

In the case of surfaces and interfaces, in particular in semiconductor systems, a possible approach is the repeated-slab scheme, in which an artificial periodicity is introduced into the system, in order to apply the standard methods of band theory /4/. Approaches which actually deal with the semi-infinite geometry in realistic calculations have been implemented, based on wavefunction matching /5/, or on density-matrix formulations /6/, but have not proven practical enough to be pursued extensively in interface calculations. Green's function formulations based on Dyson's equation, which have been very successful in point defect calculations, were used only in conjunction with simplified descriptions of the band structure, such as the empirical tight-binding scheme /7/. An alternative Green's function method, the Green's function matching, was proposed by Garcia-Moliner et al. /8,9/ and by Inglesfield /10/ and has until recently been used in the context of simplified pseudopotential calculations (e.g. for the Si <111> surface /11/, for the <100> and <111> surfaces and for twin faults in Cu /12/).

In the present paper we give a progress report on a new method, which combines the Green's function matching method with the self-consistent approach based on Dyson's equation. Our aim is to perform calculations for semiconductor interfaces with the

same level of realism and accuracy obtained for point defects. Starting from a local-density, self-consistent bulk band structure on a localized orbital basis, an explicit representation for the Green's function of a semiconductor-semiconductor interface is derived, in terms of the bulk Green's function of the component systems. Exploiting the localization of the basis set and the rapid fall-off of charge rearrangements near the interfaces, a self-consistency loop scheme based on Dyson's equation and on the matching method can be formulated, in full analogy with the defect problem /13/. An approach quite analogous in philosophy, but more oriented towards metallic surfaces is being independently pursued by Benesh and Inglesfield /14/.

In Section II an overview of the formalism is given. Section III is devoted to a description of the implementation of the method in the specific case of a <110> interface between zincblende semiconductors. Finally, in Section IV the feasibility of the method is exemplified by some preliminary tests on the GaAs-Ge <110> interface.

## II - DESCRIPTION OF THE FORMALISM

We begin by recalling the definition and basic properties of the Green's function operator  $\hat{G}(E)$ . Given a system described by the one-electron Hamiltonian  $\hat{H}$ , we define formally :

$$\hat{G}(E) = (E - \hat{H})^{-1} = \sum_n \frac{|n\rangle\langle n|}{E - E_n} \quad (1)$$

or, in terms of matrix elements :

$$\langle \vec{r} | \hat{G}(E) | \vec{r}' \rangle = \sum_n \frac{\psi_n(\vec{r}) \psi_n^*(\vec{r}')}{E - E_n} \quad (2)$$

where  $|n\rangle$  is a complete set of eigenstates of  $\hat{H}$ , with eigenvalues  $E_n$  and wave-functions in real space  $\psi_n(\vec{r}) \equiv \langle \vec{r} | n \rangle$ . Quantities of physical interest are obtained from the Green's function via spatial or energy integration. For example, the density of states  $D(E)$  is given by

$$\begin{aligned} D(E) &= \lim_{\epsilon \rightarrow +0} \left[ -\frac{1}{\pi} \text{ImTr} \hat{G}(E+i\epsilon) \right] = \\ &= \lim_{\epsilon \rightarrow +0} -\frac{1}{\pi} \text{Im} \int d^3 r \langle \vec{r} | \hat{G}(E+i\epsilon) | \vec{r} \rangle \end{aligned} \quad (3)$$

and the charge density is :

$$\rho(\vec{r}) = -\frac{1}{\pi} \text{Im} \int_{-\infty}^{E_F} dE \langle \vec{r} | \hat{G}(E+i\epsilon) | \vec{r} \rangle \quad (4)$$

where the limit  $\epsilon \rightarrow +0$  is always understood. We see that  $n(\vec{r}, E) \equiv (-1/\pi) \text{Im} \langle \vec{r} | \hat{G}(E+i\epsilon) | \vec{r} \rangle$  has the meaning of a density of electrons in space and energy. Finally, we recall that if the Hamiltonian of the system can be written as  $\hat{H} = \hat{H}_0 + \hat{V}$  and if the Green's function corresponding to  $\hat{H}_0$  is  $\hat{G}_0$ , then  $\hat{G} = (E - \hat{H})^{-1}$  satisfies Dyson's equation :

$$\hat{G} = \hat{G}_0 + \hat{G}_0 \hat{V} \hat{G}. \quad (5)$$

Consider now an interface between two solids, say A and B, and let us idealize its description by assuming the one-electron potential  $V_{AB}$  of the system to be :

$$V_{AB}(x,y,z) = \begin{cases} V_A(x,y,z) & \text{if } z < 0 \\ V_B(x,y,z) & \text{if } z > 0 \end{cases} \quad (6)$$

Here the  $z = 0$  geometrical plane is identified with the interface, and the bulk periodic potentials  $V_A, V_B$  of the two media are introduced. The matching formalism provides an explicit expression for the one-particle Green's function  $\hat{G}_{AB}^0$ , corresponding to the potential (6) in terms of  $\hat{G}_A$  and  $\hat{G}_B$ , corresponding respectively to the bulk A and B systems. In order to reproduce these expressions here we must specify some notations. We shall consider the interface restriction of  $\hat{G}$ , which we denote by  $G$ , and which has matrix elements of the type  $\langle \vec{r}_s | G | \vec{r}'_s \rangle$  only, where  $\vec{r}_s = (x_s, y_s, 0)$ . We shall also use a special notation for the normal derivatives of  $\hat{G}$  /8,9/ on the interface, i.e. when both arguments approach the interface :

$$\begin{aligned} \pm G^\pm &= \lim_{z \rightarrow \pm 0} \frac{\partial}{\partial z'} \langle \vec{r} | \hat{G} | \vec{r}' \rangle \Big|_{z'=0} \\ 'G^\pm &= \lim_{z' \rightarrow \pm 0} \frac{\partial}{\partial z} \langle \vec{r} | \hat{G} | \vec{r}' \rangle \Big|_{z=0} \end{aligned} \quad (7)$$

We then find, for the interface projection  $G_{AB}^0$  the expression /8/ :

$$(G_{AB}^0)^{-1} = G_B^{-1} ({}^-G_B^0) - G_A^{-1} ({}^+G_A^0) \quad (8)$$

and, for the three-dimensional  $\hat{G}_{AB}^0$  :

$$\begin{aligned} \langle \vec{r} | \hat{G}_{AB}^0 | \vec{r}' \rangle &= \langle \vec{r} | \hat{G}_A | \vec{r}' \rangle + \langle \vec{r} | \hat{G}_A G_A^{-1} (G_{AB}^0 - G_A) G_A^{-1} \hat{G}_A | \vec{r}' \rangle \\ &\quad \text{for } z \text{ and } z' < 0 \\ \langle \vec{r} | \hat{G}_{AB}^0 | \vec{r}' \rangle &= \langle \vec{r} | \hat{G}_B | \vec{r}' \rangle + \langle \vec{r} | \hat{G}_B G_B^{-1} (G_{AB}^0 - G_B) G_B^{-1} \hat{G}_B | \vec{r}' \rangle \\ &\quad \text{for } z \text{ and } z' > 0 \end{aligned} \quad (9)$$

and similar equations for the case when  $z$  and  $z'$  are on opposite sides of the interface /8/. It is possible to show that Eq.(9) can be obtained from the Dyson equation considering  $\hat{G}_A$  as unperturbed Green's function and  $[V_B(\vec{r}) - V_A(\vec{r})]\mathcal{G}(z)$  as a perturbation extended to the half-space  $z > 0$ .

We shall now take these results as a starting point for a realistic description of the interface, i.e. one in which actual charge and potential rearrangements at the interface are self-consistently taken into account. To accomplish this goal, in analogy with the treatment of defects in semiconductors /1,2/ we take  $\hat{G}_{AB}^0$  as a starting point in a Dyson equation to be iterated to self-consistency. One can compute the charge density  $\rho_{AB}$  from  $\hat{G}_{AB}^0$ , derive from it a potential  $V_{AB}$  in the local density approximation, subtract from it the idealized potential (6) to obtain the starting "defect" potential  $\Delta V_{AB}$ , to be inserted in Dyson's equation

$$\hat{G}_{AB} = \hat{G}_{AB}^0 + \hat{G}_{AB}^0 \Delta V_{AB} \hat{G}_{AB} \quad (10)$$

This interface potential  $\Delta V_{AB}$  derives from charge rearrangements in a region of a few atomic planes. It is, however, in general not restricted to this region because charge transfer across the interface can produce a dipole layer resulting in a step-like component of  $\Delta V_{AB}$  extending to infinity on both sides. Therefore  $\Delta V_{AB}$  cannot be assumed to be localized; however, it is easy to see that a localized potential always results by subtracting a suitable abrupt-step potential from it (see Fig.1).

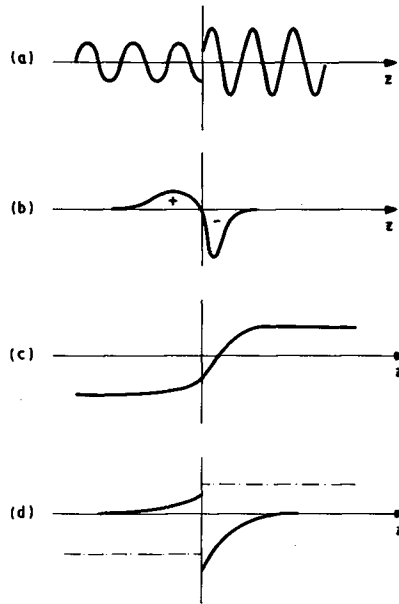


Fig.1 - (a) Schematic picture of the laterally averaged idealized matching potential (Eq.(6))  
 (b) Sketch of possible charge rearrangement near the interface and  
 (c) of the corresponding potential change  $\Delta V_{AB}$ .  
 (d) Breakup of  $\Delta V_{AB}$  into  $\Delta V_{loc}$  (solid line) and  $\Delta V_{step}$  (dash-dot line).

Therefore we can write in general

$$\Delta V_{AB} = \Delta V_{loc}(\vec{r}) + \Delta V_{step}. \quad (11)$$

The Dyson equation (10) can then be solved in two steps. First one can take care of the step potential via a new matching between rigidly shifted bulk Green's functions  $\hat{G}_A(E + \Delta V_{AB}(-\infty))$ ,  $\hat{G}_B(E - \Delta V_{AB}(+\infty))$ , to obtain a new  $\hat{G}_{AB}^S$ . Then we solve a Dyson equation for the effect of the localized potential on  $\hat{G}_{AB}^S$ :

$$\hat{G}_{AB} = \hat{G}_{AB}^S + \hat{G}_{AB}^S \Delta V_{loc} \hat{G}_{AB} \quad (12)$$

It is easy to prove that the  $\hat{G}_{AB}$  obtained from Eq.(12) is indeed the sought solution of Eq.(10). Notice that Eq.(12) only involves the localized part of the potential, and it is therefore suitable for a solution on a set of localized orbitals (after exploiting the periodicity parallel to the interface). Once  $\hat{G}_{AB}$  is obtained, we can go through the loop again, starting from the determination of a new  $\Delta V_{AB}$  to plug into Eq.(10), and repeating the procedure until the new  $\Delta V_{AB}$  coincides with the previous one up to a prescribed degree of accuracy. Notice also that the self-consistent procedure will eliminate the arbitrariness arising from the definition of the ideal potential (1), in which no prescription for the relative zeroes of  $V_A$  and  $V_B$  is given.

### III - IMPLEMENTATION OF THE FORMALISM FOR SEMICONDUCTOR INTERFACES

We shall now briefly discuss the steps which are needed to translate the formal developments of the previous Section into a practical computational method. To this aim, we shall consider as an example the <110> interface between two lattice-matched zincblende semiconductors. The first ingredient of our method is a self-consistent bulk band structure calculation on a basis of localized orbitals. This can be achieved by an ab initio pseudo-potential calculation on a gaussian-type basis /1, 15/ in analogy to most defect calculations, or by an all-electron calculation with muffin-tin-type orbitals /16/. Gaussian basis sets are quite convenient for the evaluation of overlap integrals and matrix elements. To take advantage of the periodicity parallel to the interface, Bloch-like combinations of crystal momentum  $\vec{k}_\parallel$  are formed out of orbitals centered on each atomic plane. Then the bulk Green's functions  $\hat{G}_A$  and  $\hat{G}_B$  can be expanded in this basis set :

$$\begin{aligned} < \vec{r} | \hat{G}(E) | \vec{r}' > = \\ = \sum_{\vec{k}_\parallel} \sum_{ii'} \sum_{R_\perp, R'_\perp} \phi_{iR_\perp}(\vec{k}_\parallel, \vec{r}) \hat{G}_{iR_\perp, i'R'_\perp}(\vec{k}_\parallel, E) \phi_{i'R'_\perp}(\vec{k}_\parallel, \vec{r}') \end{aligned} \quad (13)$$

where  $\phi_{iR_\perp}(\vec{k}_\parallel)$  is formed out of the orbitals of type  $i$  ( $i$  includes orbital type and position  $R_\perp$  of the atom in the interface unit cell) centered on plane  $R_\perp$ . Assuming that charge rearrangements do not extend beyond the third atomic plane on each side of the interface, and considering that there are 2 atoms per plane in the unit cell of the <110> interface, the size of the coefficient matrix  $\hat{G}_{iR_\perp, i'R'_\perp}$  is  $12 N \times 12 N$ , where  $N$  is the chosen number of orbitals per atom.

For example, with a set of 11 gaussians per atom, as used in the calculations for the vacancy in Si in Ref./1/, we have  $132 \times 132$  matrices. If we choose an extremely accurate set of 20 orbitals per atom /15/ (s, p and d orbitals, plus an additional s one, each with 2 different gaussian decay constants) the size of the  $\hat{G}$  matrices becomes  $240 \times 240$ . It is, however, extremely important to notice that most of the matrix manipulations involved in the matching procedure only concern much smaller matrices, i.e. those required to represent operators restricted to the interface. Consider indeed Eq.(13) and specialize  $\vec{r}$  and  $\vec{r}'$  to  $\vec{r}_s$  and  $\vec{r}'_s$ . Then only one plane on each side of the interface must be retained, as all other planes have atomic positions with the same projections on the  $z = 0$  plane as one of these two planes, in the <110> geometry, and therefore gaussians related by a constant factor on all points of the interface plane; other types of orbitals may not have this exact property but are to a good approximation linearly dependent on the interface plane. Another exact proportionality, on the interface plane, connects some gaussians from the same atom and with the same decay constant, but different angular momenta, e.g.  $s$ - and  $p_z$ -like functions. Thus, all matrices without a caret (^) superscript in Eq.(8) and (9) can be shown to reduce to  $48 \times 48$  or to  $32 \times 32$  size in the cases of 20 or 11 gaussians per atom, respectively. Notice also that all matrix inversions and summations over indices in matrix products in (8) and (9) concern such smaller matrices, which are quite comparable in size to those encountered in the defect calculations.

It is remarkable how much information about the system is contained in the smaller projected matrices. It is in fact easy to see from the interpretation of the imaginary part of the diagonal elements of the Green's function given at the beginning of Section II that

$$D_{\text{int}}(E) \equiv -\frac{1}{\pi} \text{Im Tr } G(E + i\epsilon) \quad (14)$$

is the local density of states on the interface plane. This holds, of course, for  $G_A$  and  $G_B$  as well as for the matched Green's function  $G_{AB}$ . Even more remarkably, for many interfaces, one can get information about the change in total density of states (with respect to the superposition of bulk A and B) from the projected matrices. Indeed, for all interfaces <lmn> which have the same density of states as their complementary < $\bar{l}\bar{m}\bar{n}$ >, the density of states can be written /17/:

$$D_{AB}(E) = \frac{1}{2} (D_A(E) + D_B(E)) - \frac{1}{2\pi} \frac{d}{dE} (\arg \det G_A + \arg \det G_B) - \frac{1}{\pi} \frac{d}{dE} \arg \det G_{AB}^{-1} \quad (15)$$

in terms of the bulk densities  $D_A$  and  $D_B$ , and of the projected Green's functions  $G_A$ ,  $G_B$  of the two materials and  $G_{AB}$ , of the interface.

The larger matrices appear in their full complexity only in Eq.(12), and in the determination of the interface potential entering it. It is hard to see how improvements in the size of this part of the calculation could be brought about. The computing and storage requirements connected with Eq.(12), however, can be handled by modern computers, since only very few matrices are involved. This is because a large fraction of the manipulations are performed on the smaller matrices. Thus one can say that in this context the main advantage of the matching formalism is to reduce (via Green's theorem /10/) a semi-infinite perturbation to a "defect potential" rigorously extending to a geometrical plane. The first of Eq.(9), e.g., has indeed the structure of the first iterative approximation to Dyson's equation

$$\hat{G}_{AB}^0 = \hat{G}_A + \hat{G}_A U \hat{G}_A, \quad (15)$$

with

$$U = G_A^{-1} (G_{AB}^0 - G_A) G_A^{-1} \quad (16)$$

being strictly localized in the  $z = 0$  plane.

#### IV - DISCUSSION OF AN EXAMPLE : THE GaAs-Ge <110> INTERFACE

In order to illustrate the feasibility of the matching procedure on a localized basis set and the information which can be obtained from the projected Green's function matrices, we describe preliminary non self-consistent results for the GaAs-Ge <110> interface at the  $\bar{\Gamma}$  point of the 2-dimensional Brillouin zone.

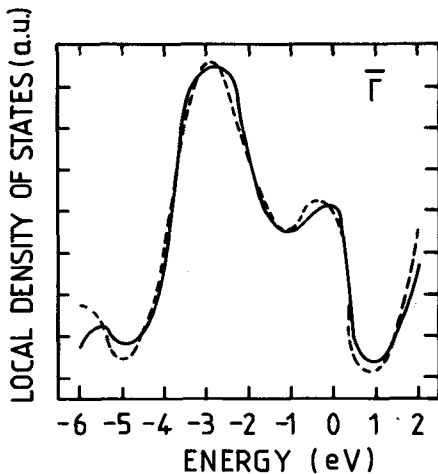


Fig.2 - Local density of states (arbitrary units) on the interface plane of a GaAs-Ge <110> interface at the  $\bar{\Gamma}$  point of the bi-dimensional Brillouin zone (solid line). For comparison, the sum of the bulk contributions (dashed line) is shown. A finite broadening is included by retaining a finite imaginary part,  $\epsilon = 0.3$  eV, in the energy.

As a starting point for our example we used bulk Green's functions obtained from an empirical potential constructed by superposing screened ionic pseudopotentials /18/, on a set of 20 gaussian orbitals per atom. Fig.2 shows the contribution of the  $\bar{\Gamma}$  point to the local density of states on the interface plane as obtained from Eq.(14) for  $G_{AB}$  and, for comparison, the bulk contribution obtained from the same equation applied to  $G_A$  and  $G_B$ . Since the calculation is not self-consistent, an arbitrary line-up was chosen, such that the tops of the valence bands of the two materials are at the same energy. It is apparent that the deviation of the interface local density of states from the sum of the two bulks is rather small in this case, in agreement with results of self-consistent slab calculations /19/.

In Fig.3 we show the deviation of the total density of states as obtained from the last two terms of Eq.(15). Although the results are limited to the  $\bar{\Gamma}$  point, excess density of states is found between 0 and -2 eV (from the top of the valence bands) and in the region between -3 and -5 eV, in fair agreement with the results of Ref. /19/.

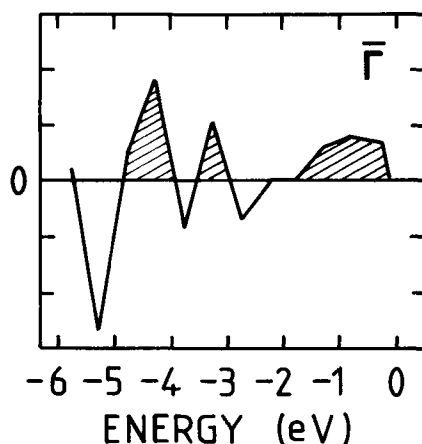


Fig.3 - Contribution of the  $\bar{\Gamma}$  point to the change in the total density of states (arbitrary units) with respect to the sum of the two bulks for the same interface as Fig.2. (see text).

In summary, we have proposed a new method for the calculation of the electronic structure of interfaces, which explicitly deals with the semi-infinite geometry of the system. A simple non self-consistent example was discussed to show the feasibility of the matching procedure on a basis adequate for realistic calculations. Self-consistent calculations for the GaAs-Ge and the GaAs-AlAs <110> interfaces are in progress.

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## DISCUSSION

D.R. Clarke: Is the formation you have discussed also applicable to the calculation of elastic stresses across interfaces of dissimilar material, and if so, has it been used for this purpose?

E. Molinari: The matching formalism is in principle applicable to Green's

functions corresponding to any Hamiltonian. In particular it can be applied to the calculation of elastic stresses across interfaces. A specific discussion of this point, which is outside the scope of the present paper, can be found in the book by F. Garcia-Moliner and F. Flores (Ref. 9).

A.P. Sutton: If intermixing were to occur at the Ge/GaAs interface the matching surface would become very convoluted. Would your method be tractable then? Would not the Pollmann/Pantelides approach be more tractable in this case?

E. Molinari: The matching formalism holds for matching surfaces of arbitrary shape, provided one defines new appropriate conventions for the A and B regions and replaces the derivatives in eq. (7) with normal derivatives with respect to the chosen matching surface (see Refs. 8 and 10). Surfaces different from planes have actually been used e.g. in defect calculations. Of course a very convoluted matching surface would not be very practical because it would not allow for taking advantage of the symmetries of the problem. Therefore in our approach the case of interface intermixing would be tractable in a simpler way by considering deviations from a sharp interface as additional local perturbations in Dyson equation (10). The Pollmann/Pantelides approach is also certainly applicable, but remains a semi-empirical approach which is not aimed at selfconsistent calculations.

M. Schlüter: Could you briefly outline, how you plan to do the self-consistency loop. You seem to have two loops in one. The local perturbation  $V$  remains only local if the correct band off-set  $E$  has been put into the "shifted" Green's functions  $G_A$  and  $G_B$ .

E. Molinari: The selfconsistency loop is outlined in eqs. (10)-(12) of the present paper. One point which is worth commenting upon in greater detail is the following: the matching procedure can be proved to be exactly equivalent to solving Dyson's equation with the perfect bulk A as the unperturbed system and with a perturbation  $V_B - V_A$  extended to the halfspace  $z > 0$ . Therefore our selfconsistency loop has the same structure as the one which has been used in previous defect calculations (Refs. 1, 2) except for the fact that Dyson's equation at each step is solved in two stages for the two contributions to the potential rearrangement (11) with respect to the unperturbed Green's function  $G_{AB}$ . Thus we only have one loop. Of course a good choice of the starting band off-set would make the self-consistent procedure much simpler, but in principle the capability of our method to lead to selfconsistency is independent of the choice of the starting off-set.