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► **To cite this version:**

A. Sutton. METHODS OF CALCULATING THE ELECTRONIC AND ATOMIC STRUCTURES OF INTERFACES. Journal de Physique Colloques, 1985, 46 (C4), pp.C4-347-C4-359. 10.1051/jphyscol:1985438 . jpa-00224689

**HAL Id: jpa-00224689**

**<https://hal.archives-ouvertes.fr/jpa-00224689>**

Submitted on 1 Jan 1985

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## METHODS OF CALCULATING THE ELECTRONIC AND ATOMIC STRUCTURES OF INTERFACES

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**Résumé** - Des méthodes pour calculer les structures électroniques et atomiques des parois, sont décrites. On donne une introduction aux pseudopotentiels et des méthodes LCAO. Des méthodes pour calculer la structure électronique d'un paroi d'une certaine structure atomique, sont considérées. On y discute la possibilité des calculations d'énergie totale, où les structures atomiques et électroniques sont calculées simultanément.

**Abstract** - Methods of calculating the electronic and atomic structures of interfaces are described. An introduction to pseudopotentials and LCAO methods is given. Methods of calculating the electronic structure of an interface with a given atomic structure are considered. The feasibility of total energy calculations, in which the atomic and electronic structures are calculated simultaneously, is discussed.

## 1 - INTRODUCTION

It is well known that the atomic and electronic structures of interfaces are intimately coupled. Coulomb interactions between ion cores in a condensed phase are moderated by the valence electron distribution which responds virtually instantaneously when ions are displaced or a different ionic species is introduced. In a metal each ion carries with it a neutralizing cloud of valence electron charge forming a neutral 'pseudo-atom'. Pseudo-atoms can be treated as single entities in those metallic systems where linear screening is valid, and their interaction is then described by an effective pair potential. But in other materials the treatment of the valence electron distribution and its response has to be more elaborate. This paper is an introduction to the theoretical methods used to study the electronic and atomic structures of interfaces involving such materials. Much of the quantitative progress in this area is founded on pseudopotentials and, in section 2, we give a brief account of the principles underlying them. A great deal of physical insight into the electronic structure of interfaces (and many other defects) has been provided relatively easily by the empirical tight binding method and other LCAO (linear combination of atomic orbitals) techniques. This method is described and appraised in the second part of section 2. With this background, we proceed, in section 3, to describe methods that have been used to calculate the electronic structure of interfaces of known (or presumed!) atomic structure. Section 4 contains a very brief account of the methods that have been used to calculate the total (internal) energy of interfaces. These are the methods which lead (at least in principle) to the minimum energy atomic configuration, with the electronic structure of the interface taken fully into account. In section 4 emphasis has been placed on semi-empirical methods because of their greater ability to deal with large numbers of atoms (e.g. for grain boundary calculations).

## 2 - FORMULATIONS OF THE ELECTRONIC STRUCTURE PROBLEM

The Hamiltonian for a system of interacting electrons and atomic nuclei consists of a sum of three terms. The first,  $H_n$ , is the sum of nuclear kinetic energy

operators and Coulomb interactions. The second,  $H_e$ , is the sum of electronic kinetic energy operators and Coulomb interactions, and  $H_{en}$  is the sum of electron-nuclear Coulomb interactions. Since electronic motion is so much faster than nuclear motion, electrons adjust to a ground state configuration for any particular set of nuclear positions. This enables us to separate the electronic and nuclear motions, and the Hamiltonian for the electrons becomes  $H_e + H_{en}$  (Born-Oppenheimer approximation). A further simplification follows from recognizing that valence electrons play the dominant role in chemical bonding. Core electrons are assumed to be unaffected by surrounding atoms and they are therefore assigned to their isolated atomic states. Accordingly, the problem is reduced to solving for the valence electronic states in the field of other valence electrons and the ion cores.

A simplification of the many electron problem has been achieved by the density functional formalism, /1/. In this formalism it is shown that the ground state total energy of the full many electron problem can be expressed as a unique functional of the electron density,  $\rho(\underline{r})$ . The utility of this formal result is limited by the fact that we cannot give an exact functional for the exchange and correlation energy of an interacting electron gas,  $E_{xc}[\rho(\underline{r})]$ . Indeed, finding  $E_{xc}[\rho(\underline{r})]$  is equivalent to solving the full many electron problem. Nevertheless, if  $\rho(\underline{r})$  is sufficiently slowly varying we can invoke the local density functional approximation and write

$$E_{xc}[\rho(\underline{r})] = \int \rho(\underline{r}) \varepsilon_{xc}(\rho(\underline{r})) d^3r \quad (1)$$

where  $\varepsilon_{xc}(\rho(\underline{r}))$  is the exchange and correlation energy function per electron of a uniform electron gas of density  $\rho(\underline{r})$ . Kohn and Sham /1/ showed that equation (1) reduces the many-electron Schrödinger equation to a one-electron equation:

$$\left( \frac{-\hbar^2 \nabla^2}{2m} + V_{eff}[\rho(\underline{r})] \right) \psi_i(\underline{r}) = \varepsilon_i \psi_i(\underline{r}) \quad (2)$$

where

$$\rho(\underline{r}) = \sum_{\text{occupied } i} |\psi_i(\underline{r})|^2 \quad (3)$$

and  $V_{eff}[\rho(\underline{r})]$  is an effective one-electron potential:

$$V_{eff}[\rho(\underline{r})] = \int \frac{\rho(\underline{r}') - \rho_{ion}(\underline{r}')}{4\pi\epsilon_0 |\underline{r} - \underline{r}'|} d^3r' + V_{xc}(\rho(\underline{r})) \quad (4)$$

$\rho_{ion}(\underline{r})$  is the ionic charge density.  $V_{xc}(\rho(\underline{r}))$  is the exchange-correlation potential, which is related to  $\varepsilon_{xc}(\rho(\underline{r}))$  by

$$V_{xc}(\rho(\underline{r})) = \frac{d}{d\rho} \left( \rho(\underline{r}) \varepsilon_{xc}(\rho(\underline{r})) \right) \quad (5)$$

Equations (2-4) are solved iteratively until the electron density distribution, given by equations (2) and (3), is consistent with the one-electron potential, given by equation (4). Such calculations are described as self-consistent. One role of  $V_{xc}$  is to eliminate the self-interaction of the electrons contained in the first term of equation (4), /2/. A number of forms for  $V_{xc}(\rho)$  have been tested, /3/.

As will be discussed in section 4, the local density functional approximation (equation (1)) has been very successful at describing ground state properties of various solids, such as the total internal energy. However, quite severe discrepancies with experiments have been found for excited state properties. For example, band gaps are normally underestimated by ~50%. This may indicate that there are significant many body effects which are not treated adequately by the local density approximation.

In general the one electron energies,  $\epsilon_i$ , obtained self-consistently from equations (2-4) are meaningful only if they are occupied states because only then do they contribute to the electron density and hence to the effective one-electron potential used to calculate them self-consistently. When an electron is promoted to a higher energy state the excitation energy is determined not only by the change in the single particle state but also by the reaction of the system as a whole to the excitation. The latter component is not significant in the case of a spatially extended state, but it can become very important for localised states, such as those bound to defects.

In the all-electron approach the eigenvalues and wave functions of all the electrons, including the ion core electrons, are calculated. Some of the methods with this approach use muffin tin potentials such as the KKR /4/, APW /5/ and LMTO /6/ techniques. A particularly efficient all-electron method for obtaining one-electron eigenvalues, called the SCF-X $\alpha$ -SW method, has been developed by Johnson and co-workers /7/ and has appeared prominently in the literature on temper embrittlement in recent years /8/. This method is very similar to muffin-tin approaches since the potential is spherically averaged within each atomic sphere and spatially averaged between them. The spherical and spatial averaging may be expected to be a good approximation for the potential in close-packed solids, such as pure metals. However, to study the formation of directional bonds and charge densities it is desirable to remove this constraint on the potential. In addition, total energies calculated by the SCF-X $\alpha$  method are very inaccurate because of the use of the muffin-tin approximation. This has led to some spectacular failures of the method to calculate the shapes of simple molecules such as H<sub>2</sub>O and NH<sub>3</sub>. Recent LMTO calculations /6/ drop the muffin tin approximation and give very good results for these two molecules.

Pseudopotential formulations of the Hamiltonian do not suffer from shape constraints on the potential, and they underpin much of the theoretical work on interfaces.

#### Pseudopotential Formulations

Pseudopotentials were introduced to replace the all electron eigenvalue problem (i.e. core and valence wavefunctions treated on an equal footing) by a simpler eigenvalue problem which applied to the valence subspace only. In the Phillips-Kleinman prescription /9/ this was achieved with use of the orthogonalized plane wave (OPW) method of bandstructure /10/, in which plane waves were combined with Bloch sums of core electron wave functions in such a way that each basis function,  $\chi_j$ , was orthogonal to the core states. The Hamiltonian,  $H_{ps}$  with these basis functions as its eigenfunctions and the valence electron energies,  $E_j$ , as its eigenvalues differed from the all electron Hamiltonian:

$$H_{ps} = -\frac{\hbar^2 \nabla^2}{2m} + W_{ps}(\underline{r}) + V_H(\underline{r}) + V_{xc}(\rho(\underline{r})) \quad (6)$$

$$H_{ps} \chi_j(\underline{r}) = E_j \chi_j(\underline{r}) \quad (7)$$

$V^H(\underline{r})$  and  $V_{xc}(\rho(\underline{r}))$  are the inter-electronic Coulomb and exchange-correlation potentials for the valence electrons only ( $V_{xc}$  is expressed here in the local density approximation).  $W_{ps}(\underline{r})$  is the total pseudopotential and represents the residual interaction between the valence electron and the ion cores after orthogonalization to the core states. The effective potential seen by the valence electron is then

$$V_{eff}[\rho(\underline{r})] = W_{ps}(\underline{r}) + V^H(\underline{r}) + V_{xc}(\rho(\underline{r})) \quad (8)$$

which is the effective potential referred to in equation (4).  $W_{ps}(\underline{r})$  is often written as a sum of ionic pseudopotentials, which in general are angular momentum dependent, centred at sites  $\underline{R}_\alpha$ ,

$$W_{ps}(\underline{r}) = \sum_{\alpha} \sum_l V_{ps}^{(l)}(\underline{r} - \underline{R}_\alpha) \hat{P}_{l\alpha} \quad (9)$$

where  $\hat{P}_{l\alpha}$  is the  $l$ th angular momentum projection operator with respect to the centre at  $\underline{R}_\alpha$ . Ionic pseudopotentials that are expressed as angular momentum dependent are termed 'nonlocal', whereas 'local' ionic pseudopotentials represent an average  $l$ -independent form,  $V_{ps}(\underline{r})$ :

$$W_{ps}^{local}(\underline{r}) = \sum_{\alpha} V_{ps}(\underline{r} - \underline{R}_\alpha) \quad (10)$$

Self-consistent calculations of the valence electronic structure are based on the partitioning of the effective potential represented in equation (8). The screening, represented by the last two terms in equation (8), is calculated self consistently from the valence electron density  $\rho(\underline{r})$  in the system of interest, whereas the ionic pseudopotential is fixed from the outset for a reference system (often the perfect crystal or isolated ion). Various approaches have been developed for finding 'transferable' ionic pseudopotentials, some of which are not based on core orthogonalisation. Before we discuss some of these we mention the empirical pseudopotential approach which is perhaps closest to the tight binding Hamiltonian.

In the empirical pseudopotential approach /11/ the effective potential, equation (8), is written as a sum of atomic pseudopotentials which are represented by just a few terms in a Fourier expansion. The coefficients are adjusted to agree with some experimentally determined features of the energy bands. Since one fits the screened ionic pseudopotentials in the reference system the screening is fixed and hence self-consistency is outside the scope of this approach. Only a few terms are needed in the Fourier expansion of these pseudopotentials, to obtain good fits to the interband transition energies. However, near a defect the potential cannot be represented by just a few terms in a Fourier expansion, and all fixed-screening theories are of doubtful validity where there is a dramatic change in the electron density such as at surfaces and vacancies.

A large number of self-consistent surface and interface calculations have been carried out with use of semi-empirical ionic pseudopotentials (12). The approach is to assume a functional form for the ionic pseudopotential, either in real space or wave-vector space, with a number of free parameters which are adjusted to reproduce either the observed free ion term values or the perfect crystal band structure. The fitting procedure can be performed with arbitrary forms for the pseudopotential in the core and the usual choice is to make the potential 'soft' (i.e. finite and smooth) in the core region. The reason for this choice is that a relatively small plane wave basis set is needed for convergence of the charge density with soft potentials. The valence electron charge density is calculated from equation (3) with the assumption that the pseudo-wave functions ( $\chi_j$  in equation (7)) are the real valence wave functions. But, although the valence electron eigenvalue spectrum may be fitted accurately by a semi-empirical ionic pseudopotential there is no guarantee that the valence electron wave-functions are accurately reproduced for the reference system. In addition, in attaining self-consistency soft-core pseudopotentials can suffer from overpenetration of the core region by the valence electron density when the ion is placed in an environment different from its reference system. Hard-core pseudopotentials (strongly repulsive at small  $\underline{r}$ ), on the other hand, ensure minimal core penetration

following changes of environment and therefore have a greater transferability. These factors have led to the recent development of 'norm-conserving' ionic pseudopotentials /13/ which give the true valence electron wave functions outside a core radius,  $r_c$ , as well as the correct valence electron eigenvalues. Their definition makes no reference to core electron states. The method of construction permits a continuous range from soft to hard core potentials with a trade-off between potential softness and pseudo-wave function accuracy away from the core. These potentials are non-local and have optimum transferability. They are fitted by a small set of analytic functions which facilitates their use either with a plane wave basis set for  $\underline{k}$ -space calculations or a local Gaussian basis set for real space calculations.

### LCAO Methods

The hallmark of LCAO methods is the expansion of the one-electron wave function,  $\psi_i$ , as a linear combination of atomic orbitals,  $\phi_\alpha$ :

$$\psi_i = \sum_{\alpha} c_{i\alpha} \phi_{\alpha} \quad (11)$$

where  $\alpha$  is a composite index denoting orbital type (s,p,d etc.) and the atomic site on which it is centred (for a review see ref. /14/). Each valence electron is assumed to move in an effective potential (equation (8)) that is represented in the one electron Hamiltonian (equation (2)) as a sum of atom-centred potentials. As in the empirical pseudopotential method these atom-centred potentials can be identified as screened ionic pseudopotentials. The Schrödinger equation reduces to a set of linear equations.

$$\sum_{\beta} (H_{\alpha\beta} - \epsilon_i S_{\alpha\beta}) c_{i\beta} = 0 \quad (12)$$

which requires

$$\det | H - \epsilon S | = 0 \quad (13)$$

for non-trivial solutions.  $H_{\alpha\beta}$  and  $S_{\alpha\beta}$  are the integrals  $\langle \phi_{\alpha} | H | \phi_{\beta} \rangle$  and  $\langle \phi_{\alpha} | \phi_{\beta} \rangle$  respectively. The Hamiltonian matrix elements,  $H_{\alpha\beta}$ , consist of one-, two- and three- centre interactions, some of which have the meaning of on-site energies, hopping integrals and crystal field integrals /15/. In the case of a perfect crystal the wavevector  $\underline{k}$  is a good quantum number and the eigenvalue problem, equation (10), factorises to a set of much smaller independent equations, one for each  $\underline{k}$ . The eigenvalues of these reduced equations give the band structure  $E_n(\underline{k})$ , where  $n$ , the band index, labels the different states at each  $\underline{k}$ .

In so-called ab initio calculations the integrals  $H_{\alpha\beta}$  and  $S_{\alpha\beta}$  are evaluated explicitly for an assumed set of atomic orbitals. Semi-empirical methods, such as Extended Hückel Theory, assume simple prescriptions for  $H_{\alpha\beta}$  and  $S_{\alpha\beta}$ . The majority of surface and interface LCAO calculations have used the empirical tight binding (ETB) approach which has its origins in the work of Slater and Koster /16/. This is an interpolation scheme whereby the matrix elements  $H_{\alpha\beta}$  are treated as parameters that are fitted to the energy bands (obtained experimentally or from accurate calculations) at points of high symmetry in the Brillouin zone /17/. The atomic basis functions  $\phi_{\alpha}$  are assumed to form an orthonormal set so that the overlap matrix  $S_{\alpha\beta}$  is the identity matrix.

Löwdin /18/ supplied a justification for this assumption by showing that one can always construct an orthonormal set of atomic basis functions,  $\Phi_\alpha$  from a nonorthogonal set,  $\phi_\alpha$ , by the transformation

$$\Phi_\alpha = \sum_\beta S_{\alpha\beta}^{-1/2} \phi_\beta \quad (14)$$

Slater and Koster /16/ showed that the  $\Phi_\alpha$  have the same transformation properties as the  $\phi_\alpha$  and one is therefore justified in assuming an orthogonal set. However, it is clear from equation (14) that the orthogonal set is more spatially delocalised than the set  $\phi_\alpha$ , which is familiar from the theory of Wannier functions.

In its simplest and most widely used form only one and selected two-centred interactions are retained in the tight binding approximation (e.g. /17/). Often the two-centred interactions are confined to nearest neighbours only. Having fitted the non-zero Hamiltonian matrix elements to selected points of an accurate band structure one studies the electronic structure of an unrelaxed defect by assuming the same matrix elements are transferable to the defect environment /19/. Krieger and Laufer /20/ criticised this last assumption, particularly in its application to a coordination defect such as a vacancy or a free surface, because it is tantamount to ignoring the change in the effective potential in the vicinity of the defect. The vindication of the use of a localised and approximately transferable atomic-like basis set came with the work on "chemical pseudopotentials" /21/. A defining equation for the localized atomic like orbitals was developed /21/ in which the influence of the atomic environment occurs only as a weak perturbation. This is achieved by using the valence orbitals on an adjacent atom to cancel off most of that atom's potential. These orbitals represent the exact solutions of the one-electron problem, and although they are not orthogonal they satisfy a secular equation, like equation (12), with a diagonal S matrix. The drawback is that the  $H_{\alpha\beta}$  which appear in the secular matrix are not matrix elements of the true Hamiltonian, but those of a non-Hermitian pseudo-Hamiltonian. However the pseudo-Hamiltonian becomes Hermitian when the basis functions are geometrically equivalent orbitals on different sites or sets of symmetry related orbitals.

For s-p bonded semiconductors, such as Si, Ge, GaAs etc., a "minimal basis set" is often used consisting of one s and three p atomic-like orbitals on each of the two atoms in a primitive cell (e.g. /17/). Very good fits to the valence energy bands have been obtained in this way but the lower conduction bands are less satisfactorily described. But it is crucial to have an accurate description of both the valence and lower conduction bands because they both contribute to defect states in the principal band gap. One way of improving the fit to the conduction bands is to include d-states in the basis set, but this increases severely the size of a defect computation. Louie /22/ has developed a successful method of including the effect of the d-states in covalent systems without increasing the size of the secular determinant. This method was used in ref. /23/ to study the electronic structure of the unreconstructed 30° partial dislocation core in Si, and it is expected to be used increasingly in the future.

ETB calculations are, strictly speaking, not self-consistent as the method does not make use of explicit basis orbitals, so that it cannot yield valence charge densities. The squares of the coefficients,  $c_{i\alpha}$ , of the orbitals are often treated as effective atomic charges. This is a questionable practice because, if one assumes orthogonal orbitals, equation (14) reveals that the coefficients correspond to charge distributed over several atoms, whereas with nonorthogonal orbitals the sum of the squares of the coefficients is not unity. Nevertheless this definition of the local charge density can be used to mimic self-consistency in simple models (e.g. /24/) where diagonal Hamiltonian matrix elements are considered to be charge dependent.

Finally we mention the semi-empirical self-consistent field LCAO methods of quantum chemistry such as the neglect of differential overlap methods /25/. As well as being self-consistent (without invoking the local density approximation) these methods have well-defined total energy algorithms /26/. However, I know of no application of these methods to study interfaces.

### 3 - ELECTRONIC STRUCTURE CALCULATIONS FOR INTERFACES WITH ASSUMED ATOMIC STRUCTURES

Given the atomic structure of an interface one can calculate the corresponding electronic structure by a variety of methods. In all such calculations, however, one must first decide how to deal with the loss of translational symmetry normal to the interface, and possibly parallel to it as well. In general, periodic interfaces (i.e. those which display two-dimensional symmetry parallel to the interface) are rare between crystals of different materials. Aperiodic interfaces can be studied only by cluster methods, whereby a region of the interface is modelled by a cluster of atoms with appropriate boundary conditions on the surface of the cluster (e.g. /27/). Various methods of 'embedding' these clusters have emerged in recent years /28/. Fortunately, the semiconductor heterojunctions of technological significance are characterised by very small lattice mismatches /29/. In those cases the mismatch is ignored and in 'ideal' interfaces atoms are assumed to be in their ideal crystal positions right up to the interface. Frequently, however, the mismatch at metal-semiconductor and metal silicide-semiconductor interfaces is not negligible. Louie and Cohen /30/ took the view that the existence of a continuum of free-electron-like states is the essential property of the metal at a metal-semiconductor interface. Accordingly, they modelled the Al crystal in their study of Al-Si interfaces by a jellium of appropriate density, which eliminated the difficulty of lattice mismatch. The main conclusions of this work have received support from calculations on the Al-Ge (001) interface (31) in which the jellium approximation was not made. For the rest of this section we will consider only periodic interfaces.

The loss of translational symmetry normal to the interface in a bicrystal signifies that crystal band structure methods are inapplicable. There are essentially two ways of coping with this. The first is to consider a superlattice of interfaces in which alternate slabs of 5 to 12 layers of each material, parallel to the interface, are stacked periodically on top of each other. This restores translational symmetry normal to the interface and the calculation is essentially a band structure calculation with a large unit cell. Similarly, this geometry has been used to study free surfaces, chemisorption and the early stages of interface formation (i.e. up to a few monolayers coverage) by periodically inserting vacua between 'slabs' of crystal, including chemisorbed atoms, overlayers etc. The second approach is to consider a true bicrystal geometry, and treat the interface as a localised perturbation (i.e. localised in the direction normal to the interface) of the bulk properties of the adjoining crystals. The Green's function formalism is ideally suited to this problem and has been developed successfully for surfaces and interfaces /32/. We shall briefly discuss these two approaches in turn.

Both plane wave and LCAO basis sets have been used in superlattice calculations. The self-consistent pseudopotential superlattice calculations, introduced by Cohen, Schlüter and coworkers /12/, employed semi-empirical ionic pseudopotentials and a plane wave basis set for the valence wavefunctions. Even with soft core pseudopotentials very large basis sets were needed to achieve convergence of the charge density (typically 300-600 plane waves for cells containing only 20-40 atoms). This results in enormous matrices to be diagonalised and it is computing power which limits the application of this method to cells containing greater numbers of atoms. The results of such a calculation consist of the energies and wavefunctions of all superlattice states, including any interface states, the total self-consistent charge density and charge densities of individual states and atom-resolved local densities of states. Self-



consistent superlattice calculations have been carried out with LCAO bases in refs. /33,34,35,36/. In general hard-core pseudopotentials require a prohibitively large plane wave basis set for convergence and this is the reason for using an atomic basis (e.g. /35/). Tight binding superlattice calculations have also been carried out (e.g. /37,38,39/).

The very large matrices one has to diagonalise with the superlattice method are a consequence of the fact that bulk states of the adjoining crystals are produced together with any interface induced states. In the second approach /32/ this shortcoming is avoided by first calculating the band structures of the adjoining crystals, and then focussing on the interface induced changes. These changes are readily found by a Green's function tight binding formalism once a matrix has been written down which represents the procedure of cutting two infinite solids and joining them to form a bicrystal (plus two semi-infinite free crystals which can be discarded). The Green's function formalism distinguishes clearly between interface induced and bulk states. It provides a powerful method of studying bound interface states, resonances and antiresonances within the bands, and wave vector-, atom- or orbital- resolved local densities of states. The sizes of the matrices involved in this method are determined by the range of the interface potential, which is usually much more localized than the wave functions of interface states. For example, Pollmann and Pantelides /32/ used an empirical tight binding Hamiltonian with a minimal basis set ( $sp^3$ ) and only nearest neighbour interactions to study ideal Ge-GaAs and Ge-ZnSe (100) interfaces. In that case the matrices involved were only  $64 \times 64$ , although it should be stressed that the calculations were not self-consistent. Although the matrices involved in the Green's function method are relatively small a large number of Green's functions for the perfect crystal (evaluated at different crystal wavevectors) have to be stored. This is not a serious problem with the large storage capacities of modern computers.

It is interesting that the results obtained for the Ge-GaAs (110) interface by the self-consistent pseudo-potential method /40/ and the empirical tight binding Green's function method /41/ are in qualitative agreement. The results differ slightly in the number and wave-vector dependences of the low-lying interface states. It is not clear whether these differences are due to self-consistence effects or the relatively poor representation of the conduction bands in the empirical tight binding Hamiltonian.

Pollmann /42/ has shown how overlayers, chemisorbed species, superlattices and defects at surfaces and interfaces can be treated by the Green's function formalism.

#### 4 - TOTAL ENERGY CALCULATIONS

Ideally we would be able to calculate the minimum free energy structure of an interface, taking into account self-consistently its electronic structure. Considerable progress has been made towards this goal in recent years, principally because of the use of density functional theory /1/ and greater computing power. For example, it is now possible to predict accurately not only the correct lattice parameter and bulk modulus of elemental semiconductors /43/, compound semiconductors /44/ and metals /45/ but also crystal stability and pressure induced phase transformations /43/. These calculations require only the atomic numbers of constituent elements and a subset of crystal structures as input information. Norm-conserving pseudopotentials, combined with the local density functional approximation are employed in the total Hamiltonian and the problem is solved self-consistently either in momentum space /46/ or real space /47/. Having achieved such an accurate description of the ideal crystal its application to interfaces is currently limited by computing power. The principal problem is convergence of the basis set. In order to predict, for example, the various reconstructed configurations of the Si (111) surface the total energy calculation would require an accuracy of better than 0.01eV/surface atom /48/. At present

this could only be achieved with a prohibitively large basis set of either plane waves or local Gaussian orbitals. Nevertheless, a number of total energy calculations have been performed, with limited relaxations included. Many of these calculations have probed the geometry and local bonding of chemisorbed atoms on semiconductor /36,49/ and metal /33/ surfaces, with photoelectron spectroscopy experiments providing a valuable check.

A more tractable (but less accurate) approach to minimizing the total internal energy of large systems in semiconductors has been developed by Chadi /50,51,52/, in an ETB framework. The total energy is written as

$$E_T = \sum_{n, \mathbf{k}} E_n(\mathbf{k}) + \sum_i (U_1 \epsilon_i + U_2 \epsilon_i^2) + U_0 N_b \quad (15)$$

occupied                      bonds

The first term is the band structure energy and is the sum of energies of all occupied one-electron states. The second and third terms denote the correction due to overcounting of the electron-electron interactions in the band structure energy and it also includes the ion-ion Coulomb interactions. The summation in the second term is over all bonds and  $\epsilon_i$  denotes the fractional change in bond length from the reference value in the perfect crystal. The empirical constants  $U_1$  and  $U_2$  are obtained from the condition that the total energy of the perfect crystal is a minimum at the experimentally observed lattice parameter and by fitting the bulk modulus. The tight binding interaction parameters are assumed to have an inverse square dependence on bond length /53/.  $N_b$  in the last term is the number of bonds in the system and  $U_0$  is determined from the cohesive energy of the perfect crystal. The last term in equation (15) is vital in those cases where bonds are broken or formed; in its absence the total energy would decrease monotonically with increasing atomic coordination. The energy of a defect in a system containing  $N$  atoms is given by  $\Delta E_T = E_T(N) - NE_0$ , where  $E_0$  is the total energy per atom in the perfect crystal. As in other empirical approaches, there is the question of transferability of the parameters  $U_0$ ,  $U_1$ ,  $U_2$  and the tight binding interaction parameters, from the perfect crystal, where they are fitted, to the defect environment. This can be tested only by comparison with experiment and indeed equation (15) has been surprisingly successful at predicting some reconstructed surface geometries /50/.

Bond distortions and reconstructions can give rise to charge transfer which introduces Coulomb interactions that are not included in equation (15). Although these interactions would be screened by valence electrons their effect is to reduce the degree of charge transfer which in turn affects the resultant atomic configuration. In principle, these effects could be taken account of by making the intra-atomic tight binding matrix elements charge dependent, as in ref /24/.

An expression for the force on an atom is obtained by differentiating equation (13) with respect to an atomic coordinate. Chadi /51/ has shown how the Hellmann Feynman theorem can be used to obtain a simple expression for the derivative of the band structure energy. Using this method he calculated a relaxed structure of the  $\Sigma=9$  (221),  $38.94^\circ$  [110] symmetrical tilt boundary in Si /52/.

Chadi's formulation for  $s$ - $p$  covalent solids has some similarities with that used by Masuda and Sato /54/ to calculate dislocation core structures in b.c.c. transition metals. These authors also express the total energy as a sum of a band structure term (arising from the  $d$  band only) and a short range repulsive interaction. The band structure energy contribution is formulated in real space using the local density of states on each atom, and integrating the one-electron energies to the Fermi level. The local density of states is approximated by a Gaussian fitted to the second moment /55/ and the  $dd\sigma$ ,  $dd\pi$  and  $dd\delta$  tight binding interactions are assumed to vary exponentially with the interatomic distance. The assumption of a Gaussian local density of states obliterates all the structure which this important function contains. The assumption could be avoided by using

the 'recursion method' /56/ to calculate the local density of states /57/. Alternatively, one could use the Hellmann-Feynman forces /51/ to give an exact expression in the framework of the d-band tight binding Hamiltonian, without making any assumption about the local density of states. We also note that Harrison /53/ has presented arguments, based on muffin tin orbital theory, for an inverse fifth power dependence of the d-d tight binding interactions on interatomic distance.

Finally we mention the use of valence force fields (e.g. /58/) to study grain boundary structures in covalently bonded solids /59,60/. In this approach the total energy is expressed as a sum of strain energy terms (bond stretching, bending and possibly torsion) and bond breaking energies with the perfect crystal as the reference configuration. Valence force fields have enjoyed considerable success in describing phonon dispersion relations for the perfect crystal /58/. However, their application to situations involving large atomic displacements is limited by the fact that they do not take into account electronic rehybridization. For example, Harrison /61/ has shown that the 2x1 reconstruction of the Si (111) surface is due to a balance between a net energy gain from rehybridization of the dangling hybrids, accompanying the buckling of the surface, and an energy penalty resulting from the distortion. Nevertheless, the valence force field approach is expected to be reliable when tetrahedral bonding is preserved, as in ref. /59/.

## 5 - CONCLUSIONS

Norm-conserving pseudopotential combined with the local density functional formalism are currently the most accurate method of describing the ground state electronic structure of surfaces and interfaces. In principle, total energy calculations for a diverse range of heterophase and homophase interfaces can be performed with this formalism, but in many cases the size of the calculation is prohibitively large for the current generation of computers. However, it has been argued /62/ that underestimation of the band gap by ~50%, by descriptions using the local density functional approximation, implies similar errors for the predicted positions of defect energy levels in the fundamental gap. In silicon, for example, this would imply a maximum error of  $\pm 0.3\text{eV}$  for the defect energy levels predicted by the most accurate calculations. Semi-empirical LCAO methods, such as the empirical tight binding method, can provide a good deal of qualitative insight, with a relatively small calculation. Recent improvements on the usual tight binding scheme were mentioned in section 2 and an efficient method of calculating forces on atoms in the tight binding scheme was referred to in section 4.

## ACKNOWLEDGEMENTS

I am grateful to Drs.K.W.Lodge and J.C.H.Spence and Professor J.W.Christian,F.R.S. for their comments on the manuscript. This research was funded by the Royal Society through a 1983 University Research Fellowship.

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## DISCUSSION

O.K. Andersen: A comment: Your statement that the most accurate way of performing density functional calculations is to use norm-conserving pseudopotentials is not true. The use of pseudopotentials is an additional, and in my opinion often unnecessary approximation. There exist many all electron calculations where this approximation is not made. Besides, the vast majority of density functional calculations for transition-, rare earth- or actinide systems have not made use of the pseudopotential approximation but were performed with all electron methods such as the KKR-, LMTO-, ASW-, LAPW-, or LCAO.

P. Neumann: How much would the complexity of density functional methods be increased by treating finite temperature situations (compared to classical molecular dynamic calculations)?

A.P. Sutton: If the calculations were carried out self-consistently it would be far too large (at the present time). However, the force on an atom can be quickly calculated by the empirical tight-binding total energy scheme (Chadi's scheme) and Newton's equations of motion could be solved in a molecular dynamics simulation using this force.

D.P. DiVincenzo: Does the local stress tensor remain a physically meaningful quantity in a theory containing non-pairwise interactions (for example, the LCAO technique)?

A.P. Sutton: I believe it does. There is a quantum mechanical stress theorem, which is similar to the Hellmann-Feynman theorem, due to Nielsen and Martin.

V. Vitek: The "asymmetry" in the total energy calculations of the band structure calculations is treated very carefully while the repulsive part is treated using a simple pair potential is unsatisfactory. I feel that, at least in metals, structural aspects of defects are often controlled more by the pair potential part than by the band structure part. Is the situation different in covalently bonded solids?

A.P. Sutton: I agree with you that a lot more physics seems to go into the band structure energy than the remaining terms in the empirical tight binding total energy expression. Certainly in covalent solids the change in the band structure energy is very important because of rehybridization. In transition metals the short range repulsive potential may well be equally important as the band structure energy, and it should depend strongly on interatomic separation at less than first neighbour separation.

J.R. Smith: Comment to question by Vitek. In the case of transition metals, our self-consistent all-electron calculations of surface energies indicate that the sum of the eigenvalues is only a fraction of the total energy.

S.G. Louie: Comment to question by Vitek: The sum of eigenvalues term is an important element in Chadi's empirical tight-binding total energy scheme which goes beyond pairwise interactions. This term allows for the rehybridization of the bonds at different geometries provided that they are not far from the bulk environment.

K.L. Merkle: To what extent can the density functional approach be applied to ionic solids and specifically can different charge states at the boundary be treated?

A.P. Sutton: There is no difficulty at all in treating ionic solids when the local density approach is combined with (say) norm-conserving pseudopotentials. Provided the calculation is carried out self-consistently, different charge states can be treated accurately.