

EMPIRICAL TIGHT-BINDING AND THE GREEN FUNCTION MATCHING METHOD IN
PROBLEMS OF SURFACES, INTERFACES AND SUPERLATTICES

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Recently the electronic tight-binding parameters for numerous elementary solids became available through the work of Papaconstantopoulos. The Green's Function Matching method in the form cast by F. Garcia-Moliner and V. Velasco allows the numerical calculation of the Green's function for ideal surfaces, interfaces and superlattices. In this paper we show how the method can be applied in practice. It turns out to be a computationally economic method that is very useful to study models and hypothesis in mesoscopic systems. Thus, useful physical trends can be obtained with a method which is not computationally involved. We present and discuss, here, results related to problems mentioned above.

I. INTRODUCTION

Ab initio methods like the recent developed full-potential linearized augmented plane wave method provide a very accurate tool to study the electronic structure of transition metal surfaces.¹ This type of calculations are very demanding in computational facilities. Hence it is desirable to have tools which allow comparatively simpler calculations, even at the expense of some loss of accuracy, as long as the results remains meaningful can be used as real first approximation. Empirical tight-binding models (ETB) are very useful to study transition metals without big computational effort. We present here a practical method usable for ETB models which works efficiently with relatively small computational labour. The theoretical basis is the Surface Green Function Matching Method for discrete systems.

The Green's Function Matching method (SGFM) in the form cast by Garcia-Moliner and Velasco² uses successfully the concept of transfer matrices. With the work of Papaconstantopoulos³ which have calculated the TB parameters for numerous elementary solids for s, p, and d bands and the work of Harrison⁴ which allows to calculate the d-band parameters, we can start out a program

to obtain the electronic structure in ideal surface, interface and superlattices of transition metals with a satisfactory bulk band structure. This theory uses the bulk TB parameters because any boundary modifications of them are already included within the theory.

The aim of this paper is to show how this method can be used to get electronic structure trends which are shown up by the surface, interface and superlattice calculations. To this purpose, we present results related to physics of those systems formed by transition metals like V, Nb, Ta and W.

II. THE THEORY

The central object of our calculation is the local value of the density of states projected on the different atomic layers (LDOS) at and near either the surface (SLDOS) or the interface (ILDOS). The density of states is then obtained from the imaginary part of the corresponding Green function (see eq. 12 below).

Let G and G_s be the bulk Green's functions for an infinite and semi-infinite systems, respectively. Let g and g_s be their respective surface projected Green's functions. Moreover, let P and I be the unit in the space span by the semiinfinite and surface

domains respectively. A fundamental SGFM result is²

$$G = P \left[G + G g^{-1} (g_s - g) g^{-1} G \right] P \quad (1)$$

which still have an unknown variable, the surface object g_s . This can be found from following equation,

$$(\omega - H_s)G = P \quad (2)$$

where the Hamiltonian H_s contains all the required information we need to describe the surface and ω is the energy. The tight-binding Hamiltonian is set up in the two center approximation within the language of Slater and Koster⁵. The non-zero TB parameters are either those calculated by Papaconstantopoulos³ for s, p and d bands or those obtained from the formulation of Harrison⁴ (d bands). We also use the simplifying assumption of ideal truncation to calculate the surface, interface and superlattice (001) electronic structure.

Projecting onto the space of atoms which feel the presence of the boundary (surface), we obtain

$$g_s^{-1} = \omega I - (P H_s P) (P G g^{-1}) \quad (3)$$

The equation (3) can be handle easier by using the concept of principal layers. Let $|n\rangle$ be the principal layer wave function describing the n^{th} principal layer. It is a LCAO wave function with nine s-, p- and d-like atomic functions on each atom and three atomic layers, i.e, it is a 27-dimensional vector. P can be written as

$$P = |0\rangle\langle 0| + |1\rangle\langle 1| + \dots \quad (4)$$

where $|0\rangle$ is the wave function related to the principal layer closest to the boundary, the $|1\rangle$ is the next down into the material and so on. If we take matrix elements of eq. (3) in the Hilbert space generated by the complete system of wave functions $|0\rangle$, we get:

$$\begin{aligned} g_s^{-1} &= \langle 0|\omega|0\rangle - \langle 0|H_s|0\rangle \langle 0|G_s|0\rangle * \langle 0|G^{-1}|0\rangle \\ &\quad - \langle 0|H_s|1\rangle \langle 1|G|0\rangle \langle 0|G^{-1}|0\rangle \\ &= (\omega I - H_{s00}) - H_{s01}^T \end{aligned} \quad (5)$$

where we have defined the T-matrix as $G_{10} = T G_{00}$. This equation (5) gives

us the right equation to calculate the surface projected Green's function and henceforth the surface problem is fully solved. For instance, if we wish to know how G_s projects well into the bulk, this is readily obtained when equation (1) is projected into the layer n . Hence,

$$\begin{aligned} G_{s,nn} &\equiv \langle n|G_s|n\rangle = \langle n|G|n\rangle + \\ &\quad + \langle n|G g^{-1} (g_s - g) g^{-1} G|n\rangle \\ &= G_{nn} + T^n (g_s - g) \tilde{S}^n \end{aligned} \quad (6)$$

where $G_{no} = T^n G_{oo}$, $G_{on} = G_{oo} \tilde{S}^n$ and $G_{nn} = G_{oo}$ for an ideal truncation.

The transfer matrices define above can be evaluated by a quick algorithm developed by Lopez-Sanchez et. al⁶ and Baquero⁷.

The matrix elements of the Hamiltonian, H_{nm} , that appear in eq. (5) are 3x3 supermatrices (each principal layer contains three atomic layers, since we have interaction up to third neighbours) each of whose elements is a 9x9 matrix (9 wave functions). For example:

$$H_{01} = \begin{vmatrix} h_{0-3} & 0 & 0 \\ h_{0-2} & h_{0-3} & 0 \\ h_{0-1} & h_{0-2} & h_{0-3} \end{vmatrix} \quad (7)$$

Notice that the rows are labeled with the index of the surface principal layer zero (containing atomic layers 0, -1 and -2) while the columns are indexed with the first principal layer (atomic layers -3, -4 and -5). We label principal layers with positive numbers and atomic layers with negatives ones. For ideal truncation $H_{00} = H_{nn}$ for any n . Also $h_{0-2} = h_{1-3}$, $h_{1-2} = h_{0-1}$ and so on. For third nearest neighbours interaction $h_{0-4} = h_{0-5} = 0$. To calculate H_{00} and H_{01} we need to know only h_{00} , h_{0-1} , h_{0-2} and h_{0-3} which are 9x9 matrices and can be easily written in a tight-binding language. They depend on the energy, ω , and the wave vector k .

This formulism can be generalized straightforwardly to account for interfaces and superlattices. The matrices double in size for the interface. In this case one gets:

$$G_i^{-1} = G_{S(A)}^{-1} + G_{S(B)}^{-1} - I_A H^i I_B - I_B H^i I_A \quad (8)$$

$G_{S(A)}^{-1}$ and $G_{S(B)}^{-1}$ are the surface Green's function of medium a and B respectively in the double space of the interface:

$$G_{S(A)}^{-1} = \begin{vmatrix} G_{(A)}^{-1} & 0 \\ 0 & 0 \end{vmatrix} \quad (9)$$

where $G_{(A)}^{-1}$ is the surface Green's function for medium A calculated from the formula (5). It is a 27x27 matrix while $G_{S(A)}^{-1}$ is 54x54. $I_A H^i I_B$ and $I_B H^i I_A$ are also 54x54 matrices of the same form of (9):

$$-I_A H^i I_B - I_B H^i I_A = \begin{vmatrix} 0 & -\tau_A H^i \tau_B \\ -\tau_B H^i \tau_A & 0 \end{vmatrix} \quad (10)$$

They describe the interaction between the two media. $\tau_A H^i \tau_B$ and $\tau_B H^i \tau_A$ are 27x27 matrices. In our model they take the form similar to the surface Hamiltonian H_{01} and H_{01}^+ respectively but with tight-binding parameters being the arithmetic average of those of the two media. This is a reasonable approximation when both sides of the interface have the same crystallographic structure and we take the same basis of wave functions.

Similar formulae can be obtained for superlattices.^{2,11} It must be pointed out an interesting practical aspect of the SGFM as applied to superlattices. It is that it separates the features of matching at each interface from those of propagation to the next interface across the slab of constituent materials. Thus the size of the matrices involved, like the secular matrix yielding the superlattice states is only double with respect to the single interface case, irrespective of the size of the supercell. Hence we can pinpoint effects of the relative thickness of the constituents for a wide variety of superlattice thicknesses avoiding the use of prohibitive amounts of computer time. The density of states is then obtained as:

$$N(\omega) = (1/\pi) \epsilon \text{Im} \int G(\kappa, \omega) d\kappa \quad (12)$$

where the integration is over the two dimensional first Brillouin zone of the interface and made by the method of Cunningham.⁸

III. RESULTS AND DISCUSSION

Figure 1 displays the s, p and d contribution to the surface density of states (LDOS) for W (001). The main contribution to the SLDOS arises from the d-band all along the whole range of energies. The s band contribution is only significant at low energies and the p band at the highest energies. This general result in bcc transition metals makes clear that to study the electronic behaviour around the Fermi level, within our model, it might be enough to use d bands only. This justifies some of our calculations (to be shown below) which were done with d bands only.

The Fig. 2 shows how the boundary effect evolves typically on moving layer by layer from the surface to the bulk for the case of W (001) and s, p and d bands. Similar result is also obtained for the d bands contribution only. We observe that already the third atomic layer present almost all of the bulk LDOS characteristics. Hence, we can say that the number of layers the surface domain includes in transition metals are close to four atomic layers. Notice, also, that the layer to layer change of the LDOS is continuous.

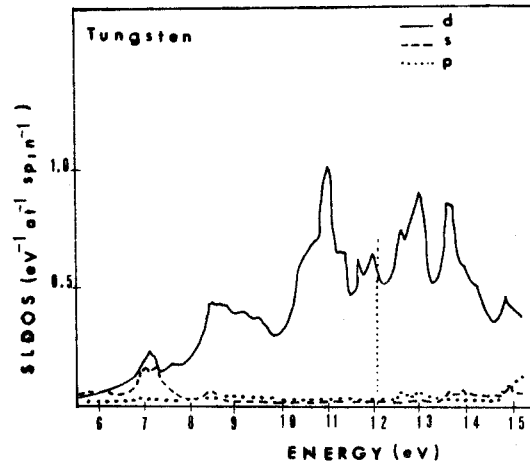


Fig. 1 The s, p and d band contribution to the SLDOS for W (001).

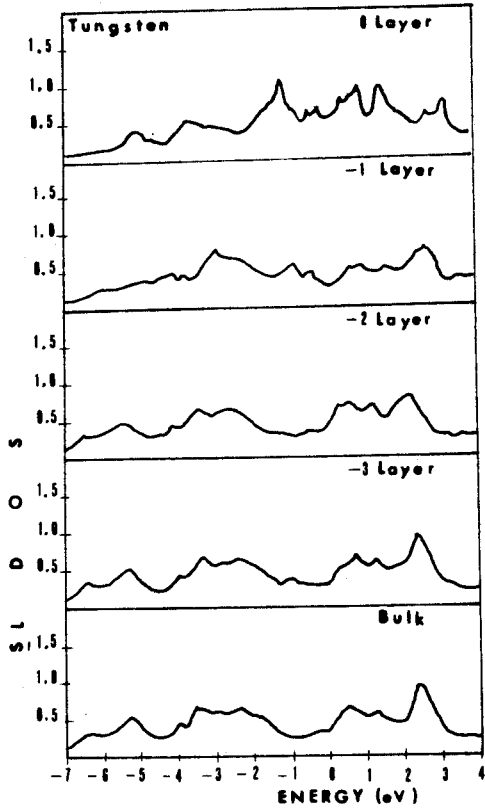


Fig. 2 The layer by layer evolution of the LDOS for W (001) and s, p and d bands.

It should be also noted that the peak with large intensity in SLDOS near the Fermi level is extremely localized as is clear from Fig. 2. It occurs only in the first atomic layer and this is a consequence of the less number of nearest neighbours at the surface. When this localized surface peak is below the Fermi level, like W. It may lead to surface reconstruction which generates a surface geometry with lower energy and the peak diminishes in intensity.⁹

The surface and bulk intensities at the Fermi energy are quite different and changes from sample to sample. This explains the difference in the surface behaviour compared to the bulk and might point out to some physical characteristics to be expected from a particular sample.

In the energy region close to the Fermi level, the bulk LDOS present a dip while the SLDOS displays some peaks of much higher intensity. This peaks are either surface states or resonances. The resonances are associated to surface levels which

goes dip into the bulk.

It is convenient to say, now, a few words about the calculation of the Fermi energy, ϵ_F . The LDOS is normalized to the nine s, p and d electrons. The bulk Fermi energy is then calculated by integrating the corresponding LDOS according to the following equation

$$\int_{-\infty}^{\epsilon_F} N_B(\omega) d\omega = d o_{spd} \quad (13)$$

where $d o_{spd}$ is the s-p-d electron occupation per atom per spin. The same integration for the SLDOS gives a lower value. This is because our calculation does not take into account automatically charge neutrality at the surface. This can be achieved by moving rigidly the LDOS until we obtain the require value for the integral. The same procedure is applied for all layers in the surface domain.

We ought to point out that on working with d bands a certain amount of charge from the s band can be transferred into the d bands. From the work of Papaconstantopoulos³ the value of this charge transfer is about one. This correction may be incorporated into the calculation at the moment of finding the right Fermi level. However, if we want to be consistently within a d-description, $d o$, should be set equal to the nominal d-occupation value. This latter procedure neglects any band charge transfer. Our d-band calculations were performed in this latter way.

The interface Fermi level, E_{FI} , is given as the arithmetic average of the bulk ones for each material, i.e., $E_{F(A)}$ and $E_{F(B)}$ respectively. This assumption takes into consideration that certain amount of charge can be transferred from one medium to the other. The Fermi level for the other atomic layers in the interface region, about four layers for each side of the interface, is supposed to vary in equal steps from E_{FI} to the bulk one on a given side.

Figure 3 compares the bulk-, the zero- and the first atomic layer LDOS at both sides of the Nb/Ta interface for a d-band calculation. Since these metals have the same lattice constant and the same crystallographic structure, stress is not important here. For each metal, the LDOS varies smoothly from layer to layer but the most significant change occurs on going through the interface where the change is abrupt. The interface reveals different characteristics according to the side we are in. Thus, for example, in the Ta

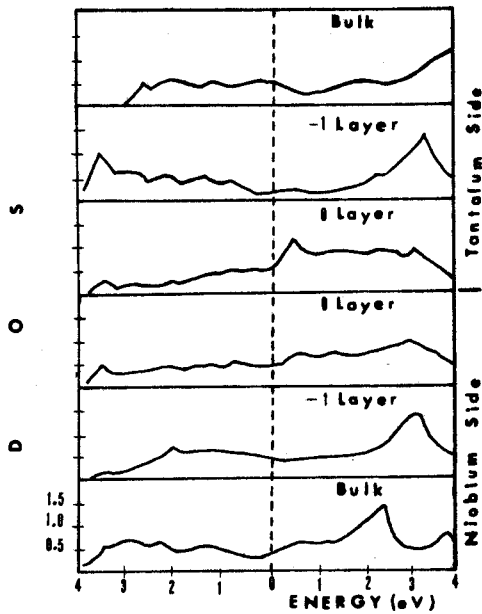


Fig. 3 The ILDOS for the first principal layer on both sides of the Nb/Ta (001) interface. The bulk LDOS is also shown for comparison. D-bands only.

side the 0-layer presents a peak of large intensity in the region close to the Fermi level ($\Delta E = \pm 1$ eV) and the structure of the three LDOS are quite distinct. However on the Nb side the 0-layer LDOS resembles more that of the bulk and the peak of large intensity is largely damped by the interface (we come back to this point below).

Figure 4 compares the Nb surface and bulk LDOS with the ILDOS arising from the Nb/V and Nb/Ta interfaces. Notices that the intensity of the surface states strongly diminishes under the influence of the other material bringing the ILDOS somewhat closer to the form of the bulk one. This maybe a consequence of the peak with large intensity in the SLDOS being below the Fermi level. This peak (or rather two resonances) is very sensitive to hydrogen absorption. Moreover Nb (001) has surface electronic properties very similar to those of W (001).¹⁰ For this reason, one might expect, like W (001), the Nb surface to accept other electrons to decrease the energy and so reduce the intensity of that peak. The Nb surface is difficult to deal with because it rapidly oxidates. The reduction of the intensity of the surface peak is not an universal fact. For instance, in

the case of Vanadium (Fig. 5), the form of the ILDOS is very little influence by the partner metal. However, it is somehow rigidly moved away from the ϵ_F . The V side for the V/Nb interface should have must of the surface electronic characteristics.

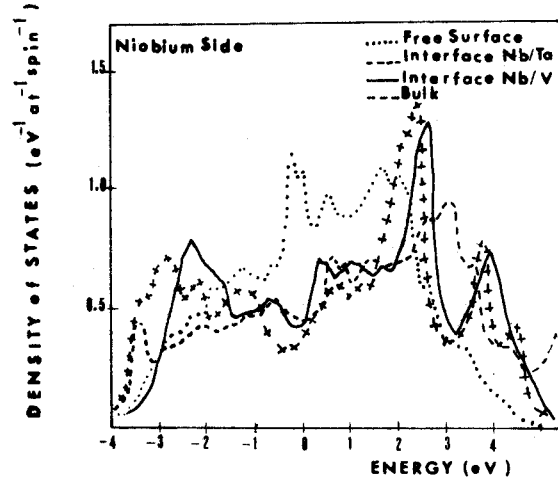


Fig. 4 The Nb ILDOS for the V/Nb and Ta/Nb (001) interfaces. The SLDOS and the bulk one are also shown. D bands only.

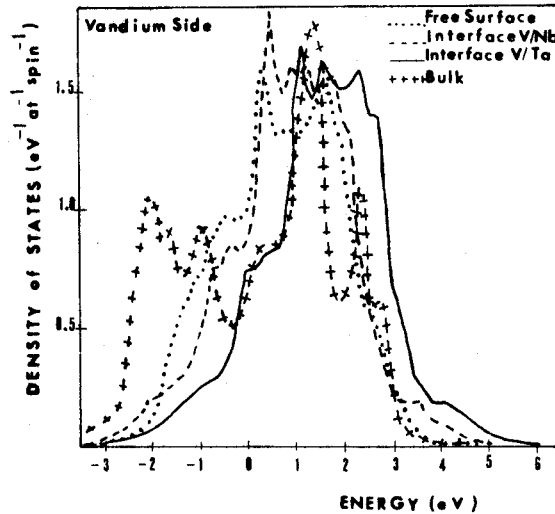


Fig. 5 The V ILDOS for the V/Nb and Ta/V (001) interfaces. The SLDOS and the bulk one are also shown. D-bands only.

From Figs. 4 and 5 it is also seen that the SLDOS and the ILDOS bandwidth is smaller than the bulk one. This is due to the less number of neighbours. This reduction does not occur in Nb ILDOS for the Nb-Ta interface. This is another manifestation the influence of the partner metal on ILDOS structure. Ta has the larger TB hopping parameters of the three metals considered in the study of interfaces. Somehow these large hopping parameters make the Nb LDOS bandwidth to increase compare to the bulk while V with the smaller set of parameters decreases it. V and Nb also reduces the bandwidth of the ILDOS of Ta. Vanadium has a strongly localized band structure.

To deal with superlattices it is required a fair estimate of the Fermi level. A fair estimate of ϵ_F is to assume that it is not very different from the interface one. For the Nb-Ta (001) interface, $\epsilon_F = -1.1$ eV. The superlattice formed by the same elements is supposed to have perfect matching and unreconstructed interfaces. This superlattice (N, N') has N principal layer of Nb and N' of Ta.

The electronic band structure was studied along the growth direction (001) for $k(0,0)$. The most significant feature is the existence, well above and below the folded bands, of a number of detached bands which depends on the slab thicknesses. Their energies at $\Gamma(001)$ and $Z(\pi/a(001))$ are given in table I for Nb-Ta (4,4) superlattice. The number of these detached bands increases with N' and is independent on N. a close look at the bands indicates that they are either above the highest or below the lowest Nb bands. Thus, they are associated with electronic states of Ta.

	E (eV)	
	Γ	Z
Highest	4.73	4.73
Highest	4.67	4.65
Highest	4.39	4.42
Lowest	-5.89	-5.93
Lowest	-6.23	-6.19
Lowest	-6.34	-6.34

TABLE I. Energies of the highest and lowest electron states at Γ and points in a Nb-Ta (001) (4,4) superlattice.

The figure 6 displays the great diversity in the spatial behaviour of the energy bands found in the calculation. four states close to the Fermi level (at -1.52 eV, -1.38 eV, -1.32 eV and -1.16 eV) for a (4,8) superlattice are used as example. In Fig. (6a) the state is confined to Ta with a dip in the middle of the slab. In Fig. (6) there is some leakage towards the Nb slab and oscillations on Ta side. In Fig. (6c) there is a strong accumulation towards the centre of the Nb slab and in Fig. (5d) the spectral strength is evenly distributed between the two materials. This spatial confinement of the different states appears in all the energy range. This is an inherently characteristic feature of the spectral phenomenology of superlattices which might significantly modulate some macroscopic properties of the components of the superlattice system.

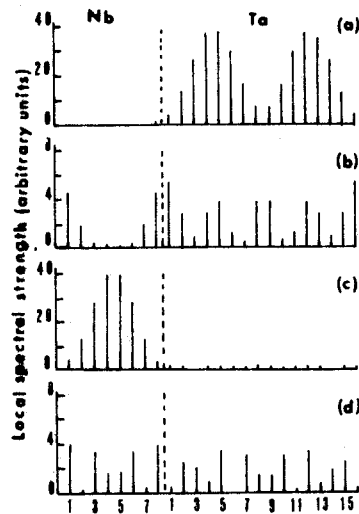


Fig. 6 Spatial variation in the spectral strength (LDOS) for four eigenstates of the same superlattice in the neighbourhood of the Fermi level for various energy eigenvalues (a) -1.62 eV. (b) -1.38 eV. (c) -1.32 eV and (d) -1.16 eV.

IV. CONCLUSION

We have shown the practical usefulness of the tight-binding models together SGFM method to study the electronic structure of transition

metal surfaces, interfaces and superlattices. The method allows the use of the bulk tight-binding parameters since the formulae explicitly account for the perturbation introduced by either the surface or the interface. The analysis shows that the main contribution to the LDOS arises from the d bands. The interface LDOS is somewhere in between the surface and the bulk one. They are quite different for the same element. The presence of the partner metal produces significant changes in the LDOS for a given metal and makes its structure to differ greatly from the SLDOS.

The model can easily be modified to include effects like stress and to introduce hypothesis related to physical situations of the type of catalysis, magnetism, etc.

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REFERENCES

- 1.- A.J. Freeman and C.L. Fu, *Magnetic Properties of Low-Dimensional Systems*, eds. L.M. Falicov and J.L. Moran-Lopez. Springer Proceedings in Physics **14**, 16 (1986).
- 2.- F. Garcia-Moliner, *Ann. Phys.* **t.2**, 179-200 (1977); F. Garcia-Moliner and V. Velasco, *Progress in Surface Science* **21**, 93 (1986); R. Baquero, V.R. Velasco and F. Garcia-Moliner, *Phys. Scripta* **38**, 742 (1988).
- 3.- D.A. Papaconstantopoulos, *Handbook of the band structure of elemental solids*, Plenum Press, N.Y. (1986).
- 4.- W.A. Harrison, *Electronic structure and the properties of solids*, Freeman, N.Y. (1980).
- 5.- J.C. Slater and G.F. Koster, *Phys. Rev.* **94**, 498 (1954).
- 6.- M.P. Lopez-Sancho, J.M. Lopez-Sancho and J. Rubio, *J. Phys. F: Met. Phys.* **14**, 1205 (1984); *J. Phys. F: Met. Phys.* **15**, 855 (1985).
- 7.- R. Baquero, ICTP-preprint IC/88/185
- 8.- S.L. Cunningham, *Phys. Rev.* **B10**, 4988 (1974).
- 9.- D. Singh, S-H. Wei and H. Krakauer, *Phys. Rev. Lett.* **57**, 3292 (1986).
- 10.- B.-S. Fang, C.A. Ballentine and J.L. Erskine, *Phys. Rev.* **B38**, 4299 (1988-11).
- 11.- V. Velasco, R. Baquero, R. Brito-Orta, F. Garcia-Moliner, *J. Phys. Condensed Matter* (1989).