Real Space Electronic Structure Calculations for Metallic Surfaces *

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The real-space (RS) linear muffin tin orbital scheme, based on the linear muffin tin orbital formalism in the atomic sphere approximation (LMTO-ASA) and on the recursion method, allows us to perform first-principles, self-consistent, density functional electronic structure calculations directly in real space. Here we show that the real space scheme can also be applied to study the electronic structure and magnetic properties of metallic surfaces and defects in these systems. To illustrate the application of this new procedure to surfaces, we use the RS-LMTO-ASA scheme to calculate the magnetic properties of an Fe overlayer on the Cu(001) surface, which have been extensively studied, using several different methods, as may be seen in the literature. We have also investigated the behavior of a substitutional Cu impurity in the Fe overlayer, since results for this system are available for comparison. We find that, as expected, our results are in very good agreement with those obtained by other methods. We note that, being implemented directly in real space, the RS-LMTO-ASA scheme does not require a high degree of symmetry. Therefore it is very flexible and can be applied in situations which are difficult to treat by other approaches. PACS Numbers: 71.10.+x, 75.30.Pd, 75.70.Ak

I. Introduction

In recent years, due to advances in preparation techniques, well defined metallic systems with bidimensional symmetry such as thin films, surfaces and multilayers have been obtained. These systems have been studied by several techniques[1], giving experimental access to physical properties which include the magnetic behavior of these systems. Simultaneously, several groups developed theoretical methods which allow one to calculate the electronic structure and magnetic properties of metallic surfaces [2-6]. Most of these ab-initio methods require perfect bidimensional symmetry, but some of the approaches allow for the inclusion of substitutional impurities or clusters of impurities in these systems[4, 7]. We note that the inclusion of steps and of defects that disturb the bidimensional symmetry of the underlying lattice have been more difficult to treat. Alternative cluster methods implemented in real space could be useful in this context, provided that the cluster is large enough to give a realistic description of the system.

The real space linear muffin tin orbital scheme (RS-LMTO-ASA)[8], based on the well known LMTO-ASA formalism[9, 10], allows us to perform first principles, self-consistent density functional calculations directly in real space. The procedure is very similar to the kspace LMTO-ASA formalism[9], but the solution of the eigenvalue problem is done directly in real space, with the help of the recursion method [11]. To avoid cluster surface effects, clusters of several thousand atoms can be used to simulate the system. The RS-LMTO-ASA scheme has been tested in several metallic systems, yielding results which agree well with those obtained using other methods. When applied to crystalline systems it gives results which are similar to those obtained from the usual reciprocal space LMTO-ASA method[8], and when applied to substitutional impurities in metals, it yields results which are in good agreement with those obtained by the KKR-GF formalims[12].

In the present work, we develop a version of the RS-LMTO-ASA scheme which can be used to study metallic surfaces. To test the new approach we apply

^{*}This paper is dedicated to Prof. Roberto Luzzi in his 60th anniversary.

the surface RS-LMTO-ASA scheme to investigate the electronic structure of an Fe overlayer on Cu(001), for which results obtained using other methods are available in the literature [4, 5, 13, 14]. We also consider the inclusion of impurities and defects on surfaces. Only recently have spin-polarized calculations of impurities at surfaces in systems involving transition metals been performed with ab-initio methods. Most of these calculations investigate the behavior of substitutional impurities (or adatoms) using the GF formalism in conjunction with KKR or LMTO approaches [4, 7]. Here, we develop a procedure which allows us to treat impurities and other local defects on metallic surfaces within the RS-LMTO-ASA scheme. To test the results, we treat a substitutional Cu impurity within the Fe overlayer, a case for which results using the LMTO-GF method are already available. The procedure used here to include impurities within the surface RS-LMTO-ASA scheme is very similar to the one used to study impurities in bulk metallic hosts[12] and, as we have shown for these systems, allows us to investigate local defects which break the structural symmetry of the lattice and are at present difficult to treat using the GF approach[15]. Therefore the surface RS-LMTO-ASA scheme presented here should be useful, not only as an alternative way of performing surface calculations, but also as a flexible approach which may enable us to study structural symmetry of the lattice. Finally we note that the surface RS-LMTO-ASA scheme can be applied, with minor modifications, to treat other systems with bidimensional symmetry, such as interfaces, sandwiches and multilayers.

The paper is organized in the following way: in section II we give a brief summary of the RS-LMTO-ASA scheme. In section III we describe the changes which have to be implemented in order to treat perfect surfaces. Results for the Fe overlayer on the Cu(001) surface are shown in section IV. In section V we discuss the inclusion of local defects and give the results for a substitutional Cu impurity in the Fe overlayer. Finally in section VI we present our conclusions.

II. The RS-LMTO-ASA scheme

Electronic structure calculations are generally begun by solving a Schrödinger-like equation for one electron in the presence of a potential that includes the interaction with the nuclei and other electrons. To solve the problem self-consistently one usually starts with an initial guess for the electronic charge density and

obtains the electrostatic potential by solving Poisson's equation for the given charge. The interaction with the nuclei and exchange and correlation terms, obtained using the local spin density functional formalism, are added. The Schrödinger-like equation is then solved and its eigenfunctions Ψ_j and corresponding eigenvalues E_i are obtained. The electrons are placed in the lowest energy states, within the restrictions imposed by the Pauli principle, and a new charge density and the corresponding effective potential are obtained. A suitable mix of old and new values is used for the potential and the procedure is repeated until the difference between the potential used when solving the Schrödinger-like equation and the one obtained from the resulting charge density differ by less than a stipulated amount. The RS-LMTO-ASA is an ab-initio method, in the sense that it follows the procedure outlined above.

Since the real-space procedure is based on the LMTO-ASA formalism, we give here a simple description of this well known and widely applied method. A more complete description of the LMTO-ASA and its various representations can be found in the literature [9, 10]. The LMTO is a linear method and its solutions are accurate near a given energy $E_{\nu},$ normally taken at the center of gravity of the occupied part of s, p or d bands being considered. In addition, the LMTO-ASA method uses the atomic sphere approximation (ASA), where the Wigner Seitz (WS) cell around each site is approximated by a WS sphere of the same volume. This approximation is very good for the closely packed metallic systems, since the shape of the WS cell is almost spherical. In the case of the open structures characteristic of semiconductors, sites with atomic number equal to zero (empty spheres) are often placed in the interstitials to make the structure closely packed. When the atomic sphere approximation is used, the LMTO calculation can be divided into a few independent steps[9, 10]. First, one finds the structure constant, a matrix that connects the several sites and mainly depend on the given structure (fcc, bcc etc...). Next is the socalled "atomic part", where one solves the Schrödinger-like equation inside each inequivalent WS sphere and obtains the potential parameters at each site. Unlike the structure constant, the potential parameters must be recalculated at each iteration, since they are associated with the potential inside the WS sphere, which changes for each iteration. Finally, the Hamiltonian is constructed using the calculated structure constant

and potential parameters. We note that when solving the "atomic part" inside a WS sphere, one normally chooses the electrostatic potential to be zero at the sphere boundary. Therefore, when constructing the Hamiltonian, one should correct the relative energy scale at each sphere by its electrostatic potential (VES). This correction includes the Madelung potential at the given site, due to the charged WS spheres associated to other sites, and also takes into account the contribution due to the charge inside the sphere itself. Finally, given the Hamiltonian, the eigenvalue problem can be solved, yielding a new charge distribution around the spheres and new potential parameters. The process is repeated until self-consistency of the potential V(r), which appears in the solution of the Schrödinger equation inside each sphere, is achieved.

The RS-LMTO-ASA scheme[8, 12, 15] is based on the LMTO-ASA formalism and follows similar steps. The "atomic part", which solves the Schrödinger-like equation within the WS spheres, is identical in the two approaches and the approximations used to treat the exchange and correlation terms are the same. In the RS-LMTO-ASA we work in the orthogonal representation of the LMTO-ASA method[10], for which the overlap matrix is close to a unit matrix. We express the orthogonal Hamiltonian H in terms of parameters of the tight-binding representation and use the firstorder approximation which neglects terms of order of $(E - E_{\nu})^2$ and higher in the Hamiltonian. It can be shown that when this is done, the eigenvalue problem has the simple form given below [8, 12], which can be solved in real space using the recursion method[11]:

$$(H-E)u = 0, (1a)$$

$$H = \bar{C} + \bar{\Delta}^{1/2} \,\bar{S} \,\bar{\Delta}^{1/2},\tag{1b}$$

$$\Psi_E = \sum_{RL} [\varphi_{l\nu}(r_R) + (E - E_{\nu})\dot{\varphi}_{l\nu}(r_R)] Y_L(\hat{r}_R) u_{RL}(E)$$
(1c)

Here $\varphi_{l\nu}(r)$ and $\dot{\varphi}_{l\nu}(r)$ correspond to solutions of the Schrödinger equation with quantum numbers L =(l,m) and its first derivative with respect to energy, for a spherical potential inside the WS sphere associated with site R, calculated at energy E_{ν} . To build the Hamiltonian we need to determine the structure constant matrix \bar{S} of the tight-binding LMTO representation[10]. This matrix, which depends on the type of lattice (fcc, bcc, hcp etc..) that one is considering, has an onsite part that connects orbitals on the same site and an off-site part which connects orbitals at different sites. The off-site part decays exponentially with the distance between the sites, resulting in a tightbinding Hamiltonian[10]. The quantities \bar{C} and $\bar{\Delta}$ are potential parameters in the tight-binding representation, which can be obtained for each orbital (l = s, p)and d) at site R, if the solutions of the Schrödinger

equation inside the corresponding WS sphere are known and the electrostatic potential VES, associated with the charges within all WS spheres, can be determined. In the RS-LMTO-ASA scheme, the eigenvalue problem is solved in real space using the recursion method[11]. A cluster of a few thousand atoms is normally used to simulate the system. Details about the implementation of the RS-LMTO-ASA scheme and the calculation of all relevant quantities mentioned here can be found elsewhere[8, 12, 15].

III. The Surface RS-LMTO-ASA Scheme

The RS-LMTO-ASA scheme described in section II can be used with minor modifications to treat crystalline metallic systems[8], impurities[12, 15] and other local defects in metals[16] and metallic surfaces, sandwiches and multilayers. There are two parts of the procedure which have to be modified to take into account the different physical situations present in these systems; the calculation of the electrostatic potential VES, which includes the Madelung term, and the way in which the Fermi level is obtained. This is clear if one compares the RS-LMTO-ASA scheme for crystalline systems with the procedure used to treat a impurity in a simple monoatomic metallic host using the same real space approach. In the case of a periodic system[8], the Fermi level is determined at each iteration of the process towards self-consistency, by filling the lowest energy states with the appropriate number of valence electrons. The resulting electronic configuration determines the charge inside each WS sphere, allows us to calculate the Madelung term using Ewald summations and therefore to obtain the electrostatic potential VES at all sites. In the case of impurities in monoatomic hosts[12], most WS spheres are neutral and significant values of charge transfer are found only in the region close to the impurity. The influence of these local disturbances is small at large distances, and VES tends to zero as the distance between the site considered and the impurity increases. As a consequence, the Fermi level is not modified by the presence of these local charge transfers and is expected to have the same value in the impurity system as in the pure host. Therefore, when treating impurities within the RS-LMTO-ASA scheme, we fix the Fermi level of the system at the value obtained for the undisturbed host. The values of charge transfers and VES at each site in the impurity region are calculated self-consistently under this constraint. Since significant charge transfers are restricted to the region around the impurity, the calculation of VES is very simple and Ewald sums are not needed.

It is known that in the vicinity of a metallic surface, a potential barrier associated with the work function prevents electrons from leaving the material. But even so, some charge can be found outside the region defined by the WS spheres of surface atoms[17, 18], and a good description of the system must take this fact into account. Therefore, when performing surface calculations within the LMTO-ASA formalism, it is usual to include one or two overlayers of empty spheres covering the surface. We note that in the RS-LMTO-ASA scheme, where large clusters of atoms are used to simulate the system, the wave function is expanded in terms of s, p and d basis functions around each site R of the cluster as indicated in Eq. 1c. The use of empty spheres provide a set of basis functions which allows us to determine, in a self-consistent manner, the distribution of charge in the vicinity of the surface.

We can now discuss the procedure used to obtain VES and determine the Fermi level in the case of perfect surfaces. All other aspects of the RS-LMTO-ASA calculations, which were described in the last section, remain unchanged. Here, as in the case of impurities in monoatomic metallic hosts[12], we expect charge transfers to be important in the region where the symmetry is broken, tending to zero as the distance of the site to the surface increases. But this bidimensional disturbance is not local, since it extends to infinity along the surface plane and, unlike the impurity case, the VES does not tend to zero at sites far from the surface [2]. A typical curve for electrostatic potential VES in the surface region is shown in Fig. 1. The value of VES will be constant for sites deep in the bulk (see Fig. 1), but this constant will depend on the distribution of charge in the layers close to the surface. This can be easily understood with a simple example. As we have mentioned, some electrons are found in the region determined by the overlayer of empty spheres close to the surface, which is negatively charged. Since the total charge must be conserved, the surface layer is often positively charged and the surface region acts as a parallel plate capacitor, changing VES at sites far from the surface and shifting the Fermi level by a constant which depends on the value of the charge transfers around the surface. To avoid shifting the Fermi level at each iteration, it is convinient to redefine the scale in order to make VES equal zero at sites far from the surface, inside the metal. In this manner, the Fermi level of the system can be fixed at the value calculated for the bulk material associated with the semi-infinite part of the metallic system being studied. Having fixed the Fermi level, one can integrate the local density of states (LDOS) and determine the charge transfer at each site, including those associated with empty spheres. Given the charges we use the bidimensional Ewald summation of Skriver et al.[2] to obtain the Madelung potential and the value of VES at each site. These codes can include effects of charge transfers, charge dipoles and quadrupoles inside the WS spheres in the calculation of VES. The dipole contribution can be significant[2], since the charge asymmetry inside the sphere can be rather large close to the surface. For example, the inclusion of dipole terms in the calculation of VES is essential to predict the value of work functions correctly. But to obtain the charge dipole inside the WS spheres, we need off-diagonal terms of the Green's function at each inequivalent site. These quantities can in principle be calculated using the recursion method[11, 19], but the computational effort increases significantly. Fortunately, the inclusion of a charge dipole inside the spheres is not important for the magnetic properties that we want to study, and for simplicity we thus neglect it here.



Figure 1. Variation of the electrostatic potential VES with depth. The depth is given by the z-coodinate, in units of lattice parameter a. The surface layer is at z = 0 and layers of atoms are placed at every integer and half integer positive z value.

As we note before, even though the sites close to the surface are perturbed in a significant manner, sites deep in the material are expected to maintain their bulk characteristics. The potential V(r), which appears in the solution of the Schrödinger equation inside the WS spheres, is for most sites very similar to that of the bulk. Since the potential parameters \bar{C} and $\bar{\Delta}$ are mainly determined by the solutions $\varphi_{l\nu}(r)$ and $\dot{\varphi}_{l\nu}(r)$ of the Schrödinger equation inside the WS spheres, they are also, for most of the sites of our large cluster, very similar to those obtained for the bulk. Here, we determine in a self-consistent manner the potential V(r) and the corresponding potential parameters for sites close to the surface but use, when constructing the Hamiltonian (see Eq.1b), bulk potential parameters for all the other sites. The use of bulk parameters does not make the procedure less accurate, since as we show below, all layers which have parameters significantly different from those of the bulk can be included in a self-consistent manner.

The first step when performing RS-LMTO-ASA calculations is to build a large cluster to simulate the system. Given the cluster, the structure constant matrix \bar{S} can be obtained and stored for future use. On a perfect surface, all sites in the same layer should be equivalent, but we must decide which layers should have their potential parameters recalculated at each iteration and which are well represented by bulk parameters. A similar problem arises in the case of impurities in metallic hosts[12], where a certain number of shells around the impurity should be treated self-consistently, while most sites in the cluster can be well represented by bulk parameters. There, a simple procedure has been developed to evaluate the number of shells to be included, and we adopt a similar approach here. We start the calculation by taking bulk values for the potential parameters at all sites, except those in the surface layer and those related to empty spheres. For these sites we use initial guesses, normally obtained assuming a plausible distribution of charge inside the spheres. Using these values and the \bar{S} matrix we construct the Hamiltonian and solve the eigenvalue problem to find the LDOS for typical sites at the surface layer and empty spheres. Then we integrate the LDOS up to the Fermi level to find the charge associated with the corresponding WS sphere. The higher moments of the LDOS, which are needed in the "atomic part" of the codes, can also be obtained. To conserve charge, any excess charge resulting from the calculation is placed on an internal layer next to the surface. The value of VES at the empty spheres and at surface sites is determined for this configuration of charge and new potential parameters are obtained. The new and old values are mixed and used to construct the Hamiltonian for the next iteration. This process is repeated until the new and the old potential parameters do not differ by more than a stipulated quantity. Then we include the next layer of atoms in the selfconsistent process and obtain the LDOS for the empty spheres and two layers of atoms close to the surface. When calculating VES, any excess charge is placed on the third layer. The process is again repeated until no significant change in the potential parameters is found from one iteration to the next. The third layer is then included in the self-consistent calculation and so on. This inclusion of layers should continue until the selfconsistent potential parameters of the last layer differ by less than a stipulated amount from those of the bulk. At this point, within the given precision, the surface is perfectly embedded in the semi-infinite metal and selfconsistency over the entire system has been achieved.

IV. RS-LMTO-ASA Calculations for an Fe Overlayer on the Cu(001) Surface.

As an application of the RS-LMTO-ASA scheme to obtain the electronic structure of metallic surfaces, we calculate an Fe overlayer on a Cu(001) surface. This system was chosen as a test ground for our procedure because it has been investigated by several different methods[4, 5, 13, 14], and these results are available in the literature for comparison. The calculation was performed using an fcc cluster of around 1300 atoms with lattice parameter a = 3.61 Å, corresponding to that of Cu. The surface, chosen to be in the xy plane, had dimensions of 8 by 8, in units of the lattice parameter. A total of 11 layers were placed along the z direction. In the first two layers we used empty spheres to allow a description of the charge distribution in the empty space next to the surface. In the third layer we placed Fe atoms and all the remaining layers were occupied by Cu atoms. Valence s, p and d electrons were considered in the calculation of a total of nine orbitals per site. A cutoff parameter[11] $L_{max} = 20$ was taken in the recursion chain and a Beer and Pettifor terminator^[20] was used. We work within the local-spin-density-functional approximation with an exchange and correlation term of the form proposed by von Barth and Hedin[21]. As in previous work[8, 12], our convergency criterium requires that the moments of the LDOS used to obtain the potential parameters for the Hamiltonian do not differ by more than 0.001 from those obtained after the solution of the eigenvalue problem. We therefore require an accuracy of order of millielectrons for the occupation of s, p and d electrons at each site. We have calculated in a self-consistent manner the potential for the empty spheres, the Fe overlayer and two subsequent Cu layers, but since there would be no results for comparison, we did not proceed any further. We used two layers of empty spheres in our calculations, but found that after achieving self-consistency, the electronic charge on the second layer was less than one millielectron, indicating that within our precision one layer of empty spheres is



sufficient to describe the system.

Figure 2. RS-LMTO-ASA results for the LDOS at the Fe overlayer and at the two subsequent Cu layers in the Fe/Cu(001) system. .

In Fig. 2 we show the RS-LMTO-ASA results for the spin-polarized LDOS of the Fe overlayer and two subsequent layers of Cu in the Fe/Cu(001) system. It is well known that the recursion method gives excellent results for integrated quantities such as occupations and other moments of the LDOS, but generally gives only the main features and not the exact values of the LDOS versus energy[11]. But even so, it is interesting to present this quantity, since it shows clearly the positions and widths of the peaks in the LDOS at each site. In Fig. 3, we present for comparison the spin-polarized LDOS at the same sites obtained by GF calculations within the LMTO method[4, 22]. Considering the limitations of the recursion approach, the agreement is in all cases excellent. In Table I we show our results for the local magnetic moment of Fe sites in the overlayer and for the Cu sites on the subsequent layers. Results for the local moments in the same system, calculated using other methods, are also shown for comparison. In the second, third and fourth lines we show results obtained using the Green's function approach within the LMTO[4, 22] and the KKR[14] formalisms. In both cases, the dipole charge around the sites, neglected in our treatment, was taken into account when calculating VES. We note that LMTO-GF results shown in the third line was obtained using the scalar relativistic approach. The results on the last two lines were obtained using the full-potential linear augmented plane wave (FP-LAPW) method in the slab configuration [5, 13]. We should note that in the FP-LAPW calculations, one monolayer of Fe atoms placed on each side of a 5-layer Cu(001) slab was used to simulate the system. We can see from Table I that our results agree well with those obtained by well established procedures. Better agreement is observed with the non-relativistic LMTO-GF calculations[17] which use a similar LMTO-ASA approach. The quality of agreement with the KKR-GF results is similar to that obtained for the case of impurities in monatomic hosts [12]. The good agreement between our results and those obtained using other methods confirms that the inclusion of the dipole of charge inside the WS spheres in the calculation of VES is not important for the investigation of magnetic properties. On the other hand, the inclusion of these charge dipoles is crucial for the calculation of work functions and, as expected, our result (8.8 eV) is too large when compared to the correct value of around 5.2 eV otained by the other methods[4, 13].



Figure 3. LMTO-GF[17, 22] results for the LDOS at the Fe overlayer and at the two subsequent Cu layers in the Fe/Cu(001) system.

Since we found very large values for the work function in our calculations, it would be interesting to compare our results for the charge transfer associated with the WS spheres, with those obtained by other methods. In Table II we present our results for these quantities, using the convention that the charge transfers is positive when the WS sphere gains electrons. As expected, the charge transfers oscillates in sign and decreases in magnitude, for sites further and further from the surface. For comparison, we also show results for the charge transfer in the Fe/Cu(001) system obtained using the Green's function approach and including charge dipoles within the WS spheres in the calculation of VES.

Reference	μ_{Fe}	$\mu_{\rm Cu}$ Surface	$\mu_{\rm Cu\ Subsurface}$
this work	2.81	0.019	-0.012
LMTO-GF[17]	2.80	0.013	-0.008
LMTO-GF[22]	2.77	0.007	-0.015
KKR-GF[7]	2.68	0.02	-
FP-LAPW[5]	2.85	0.04	-
FP-LAPW[13]	2.69	0.06	-0.01

Table I - Local Magnetic Moments, in units of μ_B , obtained for the Fe/Cu(001) system

Atom	this work	KKR-GF [7]	LMTO-GF[22]
Empty spheres	0.25	0.22	0.34
Fe overlayer	-0.38	-0.36	-0.41
Cu surface	0.14	0.15	0.07
Cu subsurface	-0.02	-0.02	0.00

Table II - Charge Transfers for the Fe/Cu(001) system.

It can be seen from Table II that the agreement between our results and those obtained by other methods is excellent. A very good agreement is also found between our results for the up- and down-spin occupation at the Fe site and those obtained from a LMTO-GF investigation of $\operatorname{Fe}_{x}\operatorname{Co}_{1-x}$ overlayer on $\operatorname{Cu}(001)$, in the limit of $x \to 0[17]$. The authors report that 5.2 electrons have spin up and 2.4 spin down, to be compared with RS-LMTO-ASA results of 5.21 up and 2.41 down electrons at the Fe site. It is clear that not only magnetic properties, but also charge transfers calculated using the RS-LMTO-ASA surface scheme agree quite well with those obtained by the well-established GF approaches. It is interesting that the electronic structure seems to be quite well described by our treatment, while the values for the work function are too large when compared to those obtained by the GF approach, and are incorrect. This can be understood if we note that, since the electronic structure and the occupations around each site are approximately the same in the two approaches, the contribution of the monopole term, associated with charge transfers, to VES is similar in the two approaches. But for metallic surfaces, the contribution of the charge dipole within the spheres to VES is typically half that of the monopole and of opposite sign, reducing drastically the value of the work function, when the same values of charge transfers are considered.

Table III - Charge Transfers around the substitutional Cu impurity in the Fe overlayer in Fe/Cu(001).

Atom	ΔQ	$\Delta Q_{\rm surf}$	$\Delta Q_{\rm local}$
Cu impurity	-0.15	-0.38	0.23
Empty spheres	0.23	0.25	-0.02
Fe overlayer	-0.42	-0.38	-0.04
Cu surface	0.12	0.14	-0.02

V. The inclusion of local defects within the RS-LMTO-ASA scheme

When a local charge disturbance is introduced in a metallic system, the electrostatic potential at very large distances is not affected [12]. So here, as in the case of impurities in metallic hosts, the Fermi level of the system does not change when an impurity, or other local defect, is introduced at the surface. Only sites close to the defect are expected to have VES, the potential V(r), and the corresponding potential parameters significantly different from those obtained for the perfect undisturbed surface. At all other sites, the values of V(r) and VES should be similar to those obtained in the absence of the impurity, and potential parameters associated with the perfect surface can be used in the Hamiltonian given in Eq.(1b). The use of these parameters here is analogous to the use of bulk potential parameters for sites far from the perturbed region in the case of impurities in monoatomic hosts[12] or with the procedure used to treat a perfect surface, as described in section III. But the unperturbed system here is considered to be the perfect surface, and in this case the WS spheres around the sites are not necessarily neutral. In the perfect surface, the sites have charge transfers ΔQ_{surf} and corresponding electrostatic potentials VES_{surf} which can be determined self-consistently. The effect of the impurity is to introduce a local perturbation relative to this previously existing configuration. To find the charge transfers ΔQ_{local} and corresponding values VES_{local} introduced by the local defect, we have to subtract from the actual charge transfer ΔQ and corresponding VES at each site the values calculated for these quantities in the absence of the perturbation. We note that the local quantities associated with the perturbation tend towards zero at

large distances from the impurity, as expected. Therefore, when treating local defects on surfaces, it is convenient to define the following relations:

$$\Delta Q = \Delta Q_{surf} + \Delta Q_{local} \tag{2a}$$

$$VES = VES_{surf} + VES_{local} \tag{2b}$$

Here the charge transfer ΔQ is written as a sum of the unperturbed perfect-surface charge transfer ΔQ_{surf} and the local charge transfer ΔQ_{local} . Since eletrostatic potentials obey the superposition principle, the value of VES associated with the actual charge transfer ΔQ can be written as a sum of VES_{surf} and VES_{local} (see Eq. 2b), associated with the perfect surface and with local charge transfers, respectively.

Now we describe in general terms the procedure used here to calculate the electronic structure around defects in surfaces. First we perform an RS-LMTO-ASA calculation for the perfect surface, in order to obtain the Fermi level, the potential parameters and the values of ΔQ_{surf} and VES_{surf} at each site. We fix the Fermi level of the system to this calculated value. We start the process with a single site calculation, where we use an initial guess for the potential parameters \bar{C} and $\overline{\Delta}$ at the impurity site, and take, for all the other sites, potential parameters obtained from the perfect (or undisturbed) surface calculation. In the case of a substitutional impurity, the structure constant \bar{S} , which depends only on the positions of the lattice sites, is not affected by the inclusion of the impurity and does not have to be recalculated. Having \bar{S} and the potential parameters for all sites, we construct the Hamiltonian of Eq.(1b) solve the eigenvalue problem to obtain the LDOS at the impurity site, and integrate this quantity up to the fixed Fermi level in order to find the charge transfer ΔQ at the impurity site. Then ΔQ_{local} at the impurity site can be easily determined using Eq.(2a) and the calculated value of ΔQ_{surf} . Again, to conserve charge in the system, the excess charge is then placed in the first shell of neighbors and the electrostatic potential VES_{local} at the impurity site is determined from the resulting local charge transfer configuration. Then VES_{surf} is added to this local value in order to obtain VES and the new potential parameters at the impurity site. The old and the new values of the impurity potential parameters are mixed and used to obtain a new Hamiltonian and find new values for the LDOS at the impurity site. The process is continued until the parameters at the impurity site are selfconsistent. Next we include the impurity and its first shell of neighbors in the self-consistent process, while the potential parameters at all other sites are kept at their unperturbed values. We note that when the impurity is placed in the surface layer, the first shell of neighbors contains three inequivalent sites: those associated with the neighboring empty spheres, those in the impurity plane, and those in the plane next to that of the impurity. We build the Hamiltonian, find the LDOS at the impurity and at the non-equivalent neighboring sites. Then we integrate the LDOS at each site up to the Fermi level to find the charge transfers. The local charge transfer at each site is obtained using Eq.(2a), any excess charge is placed in the next shell of atoms, and VES_{local} at each site is determined for this charge configuration. New values for VES and for the potential parameters are obtained and the process is continued until self-consistency at the impurity site and its first shell of neighbors is achieved. As in the case of impurities in metallic hosts, we should continue to add shells until the self-consistent values of the potential parameters obtained for the last shell included do not differ from the ones calculated for the undisturbed system, by more than a stipulated amount. For sites beyond this last shell of atoms, both VES and ΔQ should be very similar to the corresponding unperturbed values VES_{surf} and ΔQ_{surf} . Then, within the required precision, the defect will be embedded in the material and the whole system will be self-consistent.

Now we use the RS-LMTO-ASA scheme described above to obtain the electronic structure around a substitutional Cu impurity in the Fe overlayer in Fe/Cu(001). To simulate the system we used the same cluster as in section, substituting one of the Fe atoms in the overlayer by Cu. Again we have used $L_{max} = 20$ as a cutoff parameter in the recursion chain and a Beer-Pettifor terminator. The potential parameters at the Cu impurity and at the first shell of neighbors were treated self-consistently, while at all other sites of the cluster they were kept at the undisturbed perfectsurface values. The first shell around the impurity includes four empty spheres, four Fe sites on the overlayer



and four Cu sites on the sublayer just below the overlayer.

Figure 4. The LDOS at a Cu impurity in the Fe overlayer over Cu(001). Both RS-LMTO-ASA results (Fig 4.a) and LMTO-GF[22] results (Fig 4b) are presented.

In Fig. 4a we show our results for the LDOS at the Cu site, introduced as a substitutional impurity in the Fe overlayer in the Fe/Cu(001) system. For comparison, in Fig. 4b we show results for the same quantity obtained using LMTO-GF calculations for the same system[22]. As we have mentioned before, the recursion method gives only the general shape of the LDOS, but the position and shape of the peaks are very similar in the two cases, showing that the RS-LMTO-ASA scheme developed here can give a good description of the electronic structure around local defects in surfaces. In Table III, we show the charge transfers ΔQ , ΔQ_{surf} and ΔQ_{local} at the Cu impurity and its first shell of neighbors. It is interesting to note that the Cu impurity loses fewer electrons than the original Fe atom at the same site, resulting in a positive effective local charge transfer of 0.2 electrons. As in the case of impurities in metallic hosts, this effective local charge is screened by effective local charges ΔQ_{local} associated with the first shell of neighbors. Finally, we find an induced local moment of 0.04 μ_B at the Cu impurity site, in good agreement with the value of 0.06 μ_B obtained using LMTO-GF approach[22].

VI. Conclusions

We have developed a surface version of the RS-LMTO-ASA scheme, which allows us to calculate the electronic structure of surfaces and local defects in these systems directly in real space. The scheme, based on the LMTO-ASA formalism and on the recursion method, is very flexible and can address problems which may be difficult to treat with other methods. To illustrate the application of the new scheme to surfaces, we have calculated the electronic structure and related properties of an Fe overlayer on the Cu(001)surface. With the exception of the work function, the results agree well with those obtained for the same system using well established approaches. We obtain a local magnetic moment of 2.81 μ_B per atom in the Fe overlayer in good agreement with the values ranging between 2.68 μ_B and 2.85 μ_B obtained by other methods[4, 5, 13, 14] for the same system. The induced local moments in the first and second Cu layers and the charge transfers, when available for comparison, also agree well with those of other methods. As we noted, the work function is expected to be too large in the present treatment, since the contributions of the charge dipole inside the WS spheres to the eletrostatic potential VES, which drastically reduce the calculated values for the work function, were not included here. But our results suggest that all other properties, including the values of charge transfer around each site, can be well described when this contribution is neglected.

We have described how to include a local defect in the surface region using the newly developed RS-LMTO-ASA scheme and applied this procedure to obtain the electronic properties around a substitutional Cu impurity in the Fe overlayer of Fe/Cu(001). The results are in excellent agreement with those obtained using the LMTO-GF approach. We show that it is convenient to define a an effective local charge transfer ΔQ_{local} given by the difference between the actual charge transfer and the charge transfer ΔQ_{surf} of the unperturbed configuration. The quantity ΔQ_{local} , in the case of surfaces, carries information analogous to the ones normally associated with charge transfers in the case of impurities in monatomic metallic hosts. For example, ΔQ_{local} at the impurity is screened by the effective local charge of the first neighboring shell. It is also the value ΔQ_{local} which tends to zero at sites far from the perturbation.

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