CALCULATION FOR A Cu(001) SURFACE WITH AN IMPURITY ATOM

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I use a self-consistent electronic structure calculation to study the system of Cu(001) that has an impurity atom replacing one of the surface Cu atoms. The calculation makes use of the tight-binding linear muffin-tin orbitals (TB-LMTO) and is carried out in real space. I am able to derive the spin-polarized local densities of states for the impurity Cr and Fe respectively, which have peaks below the Fermi level. Charge transfers between the impurities and their neighbors also result in different distributions of magnetic moments for the two impurity systems, with the Cr having approximately $0.5\mu_B$ and the Fe atom having a negligible magnetic moment.

1. Introduction

In the article I report an electronic structure calculation of Cu(001) surface using an *ab initio* method. The surface is semi-infinite and has an impurity atom replacing one of the surface Cu atoms. Similar configuration on iron substrate has been studied[1] and is found to be stable and a starting point for alloying process. With the technique of scanning tunneling microscopy (STM), it is now possible to identify individual surface atoms with their distinctive surface spectra.[2,3] Since peaks in the spectra correspond to high densities of states of the electrons, a calculation of the surface electronic structure can indirectly serve the same purpose as of the STM. It can further be used to derive related magnetic and optical properties, which find ever-increasing applications in microelectronics.

Development of surface physics and complex materials has stimulated the research of novel methods to calculate the associated electronic structures. Having a unified and straightforward formulation is essential for a method that is aimed at the treatment of large systems. It is also imperative that the formulation lead to manageable computation task. Over the years the linear muffin-tin orbitals (LMTO)[4] developed by O. K. Andersen has been one of the most efficient method in dealing with electronic structures. Later development[5,6] has made it easier for tight-binding calculations and thus more suitable for complex systems. A real-space calculation

is also possible under such a scheme, taking advantage of the easy combination of the TB-LMTO and Green's function.

Systems with low symmetry are more easily treated in real space. Without the restrictions imposed by the periodicity as normally required in **k** space calculation, the system looks natural and the formulation can be much simpler. A method that combines the TB-LMTO and Green's function has been used in surface calculation[7] and tested for its efficiency[8] in the latest improvements of the scheme. Green's function has been chosen as an effective tool in electronic structure calculations.[1,9−14] My latest calculation[8] also indicates that the relationship between the computation time and the number of atoms involved is still linear with as many as 768 atoms included in the system. That affords us an efficient treatment of the impurity problem on Cu(001).

2. Method of Calculation

The method has its origin in the LMTO method under the atomic sphere approximation (ASA).[15] The ASA greatly simplifies the formulation and offers accurate results for many systems, such as the metal surface when surface relaxation can be neglected.[16] Under the ASA, the orbitals are connected to the envelope function K which is the regular solution of the Laplace equation, centered at **R**,

$$K_{\mathbf{R}L}(r_{\mathbf{R}}) = (r_{\mathbf{R}}/w)^{-l-1}Y_L(r_{\mathbf{R}})\,, \tag{1}$$

where w is the average Wigner–Seitz radius. K can be expanded in the atomic sphere at $\mathbf{R}'$ as the following,

$$K_{\mathbf{R}L}(r_{\mathbf{R}}) = -\sum_{L'}(r_{\mathbf{R}'}/w)^{l'}\frac{Y_{L'}(r_{\mathbf{R}'})}{2(2l'+1)}S_{\mathbf{R}'L',\mathbf{R}L}$$

$$= -\sum_{L'}J_{\mathbf{R}'L'}(r_{\mathbf{R}'L'})S_{\mathbf{R}'L',\mathbf{R}L}\,, \tag{2}$$

where J is the irregular solution of the Laplace equation and **S** is the structure matrix, which can be independently calculated regardless of what actually occupy the atomic spheres. With the formulation carried out in real space the geometrical structure of the system is built into the calculation in the most natural way. According to Andersen *et al.*[5,6] a tight-binding scheme can be derived by reducing the amplitude of the envelope function from inside each of the atomic spheres with proper chosen cutting parameters $\bar{\mathbf{Q}}$,

$$\bar{\mathbf{J}} = \mathbf{J} - \mathbf{K}\bar{\mathbf{Q}}\,. \tag{3}$$

The new so called screened envelope function can be expressed as the following matrix,

$$\bar{\mathbf{K}}^{\infty} = \mathbf{K} - \bar{\mathbf{J}}\bar{\mathbf{S}}\,. \tag{4}$$

$\bar{\mathbf{K}}^{\infty}$ and $\bar{\mathbf{J}}$ are now matched with the orbitals, which are a linear combination of wave function φ_{ν} and its energy derivative $\dot{\varphi}_{\nu}$, both calculated at a fixed energy

value E_ν within the framework of the density functional theory[17,18] and local density approximation (LDA). The matching coefficients are now parts of the Hamiltonian and overlap matrix of the system. An orthogonalizing process can further eliminate the presence of the overlap matrix. The Green's function now takes on the simple form,

$$G(z) = (z - H)^{-1},\qquad(5)$$

where H is the Hamiltonian of the system after orthogonalization. The local density of states (DOS) $D(E)$ can be calculated from the following equation,

$$D(E) = -\frac{1}{\pi}\lim_{\epsilon\to 0}\text{Tr Im }G(E + i\epsilon),\qquad(6)$$

where Tr and Im denote the trace of the imaginary part of Green's function $G(E + i\epsilon)$.

The calculation of DOS may look daunting since it demands repeated inversions of large complex matrices. With the help of a set of recursive equations,[19,20] however, direct inversion can be avoided. Results are derived faster from a series of operations involving only much smaller matrices, which are divided blocks of $G(E + i\epsilon)$. One advantage of using this scheme is that the recursive Green's function has the flexibility needed in treating a complex system. Portions of the system can be targeted for calculation while others are ignored without jeopardizing the accuracy of the selected local physical properties.

Self-consistency procedures also help shorten the computation cycle. Through a scaling process, automatic adjustments of the potential parameters and energy value E_ν are enacted in the repeated calculations of wave function φ_ν and its energy derivative $\dot{\varphi}_\nu$. The potential inside each atomic sphere includes the nuclear, Hartree, Madelung and exchange-correlation potential under the LDA and important Darwin corrections. A new round of DOS calculation can be started with the output potential parameters from the scaling. But a third round is usually not necessary, given the rapid convergence of parameters from the scaling procedures.

3. Results of Calculation

The system that is actually put into calculation has a total of 12 layers of atomic spheres including two empty overlayers, which are prepared for charge extension out of the surface layer. Each layer has 32 atomic spheres and is divided into four chains. Since previous calculations indicate that six layers below the layer targeted for convergent DOS are needed in the system, a total of 12 layers are assembled for adequate results of DOS in the top six layers.

Figures 1(a) and 1(b) are the calculated DOS of the Cr atom on Cu(001), with 1(a) representing the majority spin and 1(b) the minority spin. Figure 1(c) is the combined DOS for both spins. Shown in Fig. 1(a) is a peak 0.95 eV below the Fermi level for the majority spin. For the minority spin, a peak is located 0.68 eV below the Fermi level. Both are far lower in energy than the peak reported[2] for a pure
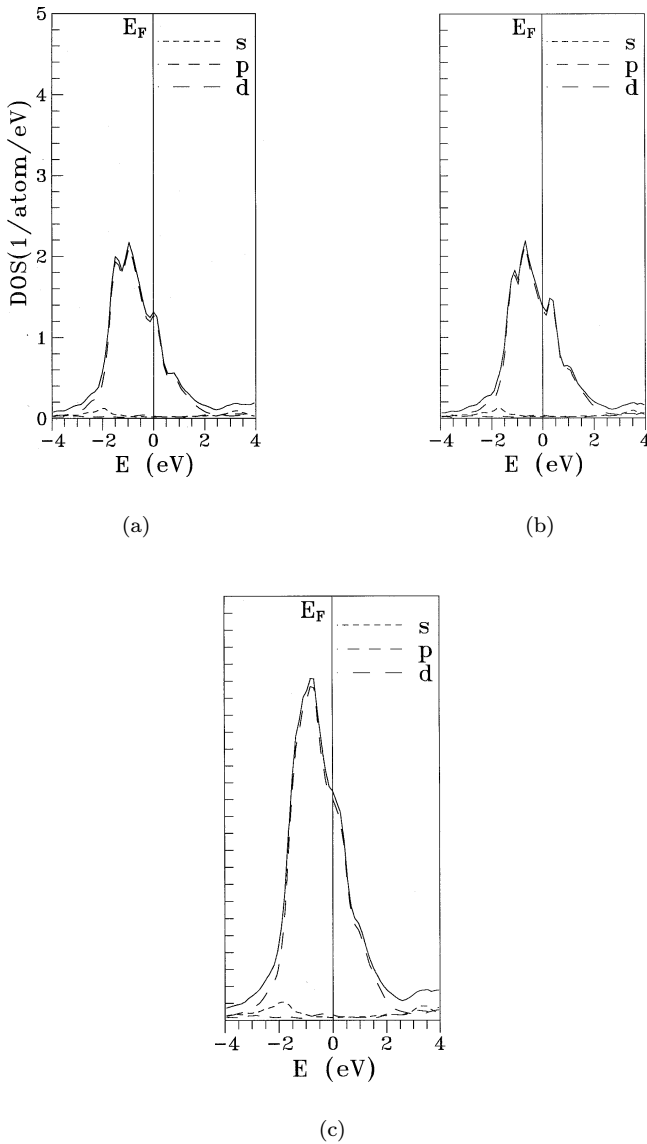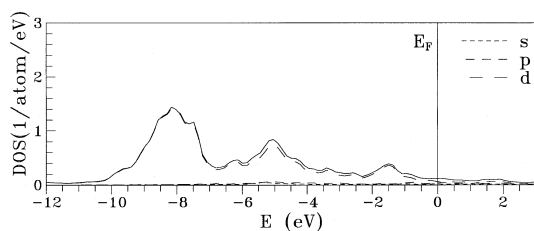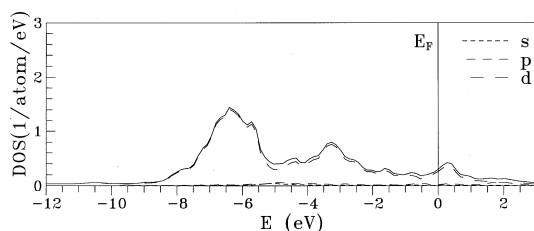
Fig. 1.   Local density of states of the impurity Cr atom on Cu(001) surface for (a) majority, (b) minority, (c) both spins.
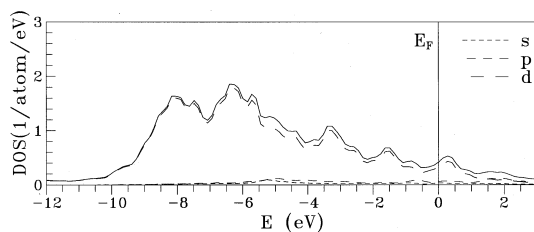
Cr(001) surface as being -0.05 eV. They are also lower than the peak at -0.3 eV reported for a single Cr on Fe(001).[3] However, both peaks should be easily identified against the background of the surrounding Cu atoms on the same surface, whose DOS are displayed in Figs. 2(a)–2(c) for the majority, minority, and combined spins respectively.

Fig. 2.   Local density of states of the surface Cu surrounding the impurity Cr for (a) majority, (b) minority, (c) both spins.

Substantial charge transfers are found between the impurity Cr, its nearest neighbors on the surface and the empty spheres above the surface. Shown in Table 1, instead of losing 0.87e as was calculated for a pure Cr(001) surface,[21] the impurity Cr atom receives 0.98e, mostly from its four nearest neighboring Cu atoms on the same surface. It is suggested that overlap of individual $3d$ energy levels between the Cr atom and its neighbors creates local levels which are lower in energy and attract nearby electrons. For nearest neighbors right above the surface, each of the four equivalent empty spheres gains 0.55e. Also listed in Table 1 are magnetic moments of the impurity Cr and neighboring Cu. The Cr has a magnetic moment of $0.52\mu_B$ and each of the four neighbors on the surface has about $0.33\mu_B$. Together they form a paramagnetic island on the surface.

Table 1.   Charge transfers between the Cr atom on Cu(001) and each of its nearest neighbors on and right above the surface.

Atomic sphere	Total charge transfer (e)	magnetic moment (μ_B)
Cr	0.98	0.52
Cu	−0.94	0.33
Empty sphere	0.55	0.00

Figure 3 gives the DOS for each of the four nearest neighbors below the Cr atom. It differs little from that of the same layer in a pure Cu(001) system. Surface effects are not strongly felt at this layer and the presence of an impurity alone does not have much disturbance. Shown in Fig. 4 is the DOS for each of the four nearest empty spheres. Mostly made up of *s* and *p* waves, the DOS looks familiar for an empty layer where electrons are loosely bound.
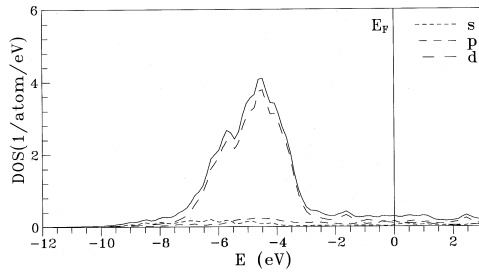

Fig. 3.   Local density of states for each of the four nearest Cu atoms below the Cr.
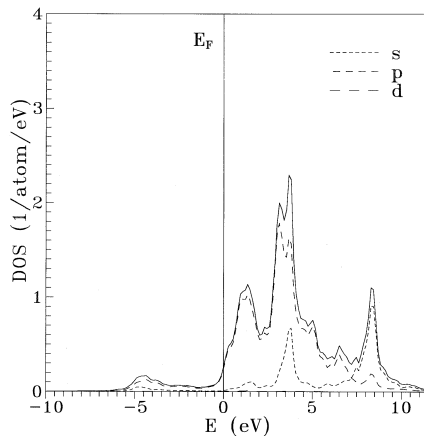

Fig. 4.   Local density of states for each of the four nearest empty spheres above the Cr.
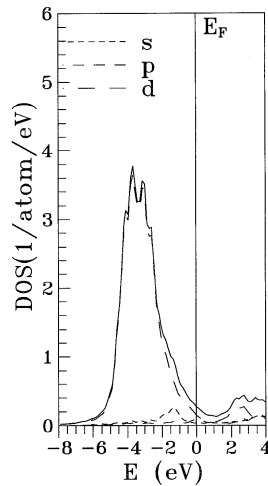
Fig. 5.   Local density of states of the impurity Fe atom on Cu(001).

Table 2.   Charge transfers between the Fe atom on Cu(001) and each of its nearest neighbors on and right above the surface.

Atomic sphere	Total charge transfer (e)	magnetic moment (μ_B)
Fe	1.43	0.04
Cu	-0.98	0.28
Empty sphere	0.48	0.00

Compared with the Cr, the DOS of Fe on Cu(001) has a distinctive feature. As shown in Fig. 5, the DOS of the impurity Fe for both spins has two spikes. Situated at 3.67 eV below the Fermi level respectively, the peaks are similar in shape to the DOS of atoms on a pure Fe(001) surface,[2] although their positions are shifted considerably from the original values. Most interestingly, the impurity Fe is virtually nonmagnetic, as shown in Table 2, while each of the surrounding Cu atoms on the surface has a moment of $0.28\mu_B xd$. Also from Table 2, the Fe atom collects 1.43e from neighboring atoms. Clearly, heavy charge redistribution due to the presence of impurity is a deciding factor in local magnetism. With no long range magnetic order present, a simple exchange of charge has the energy levels for both spin of the Fe atom occupied equally.

4. Conclusions

By combining TB-LMTO and Green's function we are able to calculate the electronic structure in real space efficiently. The method is thus suitable for systems with reduced symmetry. Although the method has its share of errors

from the employment of the LDA and ASA, it offers easy formulation and provides reasonable results for a few known systems, requiring only modest computation resources. In the article we are presented with spin-polarized local DOS of impurities on Cu(001) and their exchange of charges with neighboring atoms. We observe peaks of DOS associated with each impurity. They could be important for surface identification and characterization and alloying process. Interesting local magnetism is also deduced from the calculation, offering one more example of the method's ability of treating local problems.

Acknowledgments

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