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The Calculation of Surface States in Real Space and An Application to Fe(OO1)

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We develop a real-space method for the calculation of surface electronic structure. The approach is based on the linear muffin-tin orbitals and recursive Green's function and can achieve self-consistency efficiently. As an application, the local density of states of Fe(OO1) system is calculated. We obtain a few surface states above and below the Fermi level. The locations of these states are in good agreement with experimental results.

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The determination of surface states is very important for research in many physical systems. The surface states decide the work function and are closely related to surface adsorption, movement of adatoms, and some important optical properties. Theoretically, one can calculate the surface electronic structure by various schemes to construct a realistic picture of how the electronic states are distributed in the surface layers. The development of an efficient and accurate method of calculation to achieve that purpose has thus been always actively pursued.

In this paper we try to use an *ab initio* calculation to work out the local density of states (DOS) of Fe(OO1) in a systematic and fairly simple manner. Recently, experimentalists have begun to probe the surface electronic structure using the scanning tunneling microscope (STM). They are able to record prominent surface states near the Fermi level. It will be shown that our calculation can connect the DOS to the STM spectra [1] and photoemission experiment [2] to a high degree and can serve as an efficient and useful model for further investigation into the surface electronic structure.

The calculation is carried out in real space and is an outgrowth of the method proposed by Yang, Cheng, Dy, and Wu for the Cu(110) surface [3]. It has since been modified to simplify the procedures involved and to make the formulation an exact correspondence to the real system. It is based on the tight-binding linear-muffin orbitals with the atomic sphere approximation (TB-LMTO-ASA), as developed by Andersen [4] and was later applied by Skriver and Rosengaard [5-6] in their study of surface systems. Due to Andersen, Jepsen, and Glötzel, the LMTO method that used to be applied in k space was formulated anew in real space [7], with screened orbitals adopted to make the formulation of Hamiltonian more efficient.

We first have to obtain the so called potential parameters that are to be used in the formulation of the system in real space. Naturally, the parameters are subject to changes in the subsequent self-consistent calculations. To begin with, a band structure calculation of Fe crystal is carried out. This is a standard self-consistent k space calculation which results in very accurate band structure and DOS for combined majority and minority spins. The (bulk) parameters thus derived are such that they differ not much from those representing the atoms a few layers below the surface and they serve as a good guess for the parameters of surface atoms. We also have to construct the system of Fe(OO1) surface. This is done by assembling 15 layers of Fe atoms and one layer of empty spheres above the surface layer of Fe. Each layer contains 25 Fe atoms, or empty spheres, if the layer is in the vacuum. The geometric part of the formulation is separately calculated, which is one of the advantages of the LMTO method, and it corresponds exactly to the real system of a semi-infinite surface, with a two-dimensional boundary condition imposed upon each layer. By doing so, the surface properties are built into the formulation even before the Hamiltonian is calculated. When the potential parameters and the geometric structure of the system are combined under the formulation of real-space LMTO, we obtain the Hamiltonian for the system.

We then come to the second stage in which the local DOS is calculated. We first define the Green's function G(z) as

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

where z is a complex number and H is the Hamiltonian of the system. The density of states D(E) can then be obtained from the following equation,

$$\mathrm{D(E)} = -\frac{1}{\pi} \lim_{\epsilon \to 0} Tr\mathrm{I}mG(E + i\epsilon), \tag{2}$$

where Tr and Im denote the truce of the imaginary *part* of $G(E + i\varepsilon)$. The inversion of the matrix is not an easy task since there are now 400 atomic spheres in the system. So we turn to the theory that was developed by Dy, Wu, and Spratlin [8]. Consider first a small system with Hamiltonian $H^{(n)}$ and Green's function $G^{(n)}$ which can be easily calculated using direct inversion. We next change the system by adding to it a layer of atoms. The Hamiltonian for the larger system now becomes:

$$H^{(n+1)} = \begin{pmatrix} H^{(n)} & V \\ V^{+} & h \end{pmatrix}, \tag{3}$$

where h is the Hamiltonian of the added layer and V is the coupling of the layer to the subsystem. Then, using the recursive equations, the Green's function $G^{(n+1)}$ of the enlarged system can be calculated by

$$G^{(n+1)} = \begin{pmatrix} G_{11}^{(n+1)} & G_{12}^{(n+1)} \\ G_{21}^{(n+1)} & G_{22}^{(n+1)} \end{pmatrix}, \tag{4}$$

where,

$$G_{22}^{(n+1)} = [(z-h) - V^{+}G^{(n)}V]^{-1}, \tag{5}$$

$$G_{12}^{(n+1)} = G^{(n)}VG_{22}^{(n+1)}, \tag{6}$$

$$G_{21}^{(n+1)} = G_{22}^{(n+1)}V^{+}G^{(n)}, \tag{7}$$

$$G_{11}^{(n+1)} = G^{(n)} + G_{12}^{(n+1)}V^{+}G^{(n)}. \tag{8}$$

These equations specify how a large system, and hence a large matrix for the Hamiltonian, can be manipulated with smaller subsystems which are easily calculated with standard procedures. The recursive Green's function has been used for years [9-11]. However the new approach has distinctive features that make it very suitable for low symmetry systems. The detail explanations can be found from Wu, Cocks and Jayanthi [12] as well as Ref. 3.

Finally the calculation has to go through the self-consistent procedures, A new set of potential parameters can be derived from the DOS produced by the recursive equations. Through a process called canonical scaling [13], the DOS of each layer is adjusted with the constraint that the whole system remains neutral. The Madelung potential term in the wave function calculation allows the exchange of charges between the atomic spheres in different layers. This charge transfer in turn affects the adjustment of DOS, especially of those in the surface layer and vacuum. When the first-order moment of DOS vanishes we obtain a new set of parameters to be put back in the system Hamiltonian and Green's function for another round of DOS calculation. The self-consistency is considered attained when the parameters no longer have significant changes.

We now examine the local DOS of four atomic spheres, each at a different layer. In Fig. 1 the DOS of the empty sphere is shown. The distribution of the states are such that they are largely located above the Fermi level, consistent with the fact that electrons extending out of the surface are more like free electrons and tend to have higher energy values. It is also obvious both from the figure and Table I that the s and *p waves* contribute most to the states in vacuum. Given that the d wave is much more localized than the *s* and *p waves we* think the extension of d wave into the vacuum is negligible, as was witnessed in the calculation of Cu(110)[3].

The DOS of three Fe atoms in the three different layers starting from the surface layer downward are shown from Fig. 2 to Fig. 4 respectively. We notice the DOS evolves from the surface pattern to that of the bulk as we go deeper into the interior. We also find that surface effects are largely limited to the empty layer and the surface layer. The charge transfer below the surface layer is almost zero, as the third and fourth rows of Table I show.

The sharp increase in tunneling conductance measured by experiment [1] occurs at 0.17 eV above the Fermi level. By inspecting Fig. 2 we can immediately identify a spike of DOS right above the Fermi level which is responsible for the resonance tunneling. This calculated peak is located 0.10 eV above the Fermi level, which agrees well with the experiment within the resolution of the calculation. There are two more peaks in Fig. 2, which appear below the Fermi level. One is located at -1.8 eV, exactly the same as the value calculated in Ref. 1. Another peak can be found at a lower energy value of -2.4 eV, which is confirmed by the angle-resolved photoemission [2] that puts the state at 2.5 eV

TABLE 1. Charge transfer between the four layers shown from Fig. 1 to Fig. 4.

Layer	Total charge transfer	Contributions from partial waves	
1	0.70	s	0.29
		p	0.36
		d	0.05
2	-0.77	s	0.51
		p	0.46
		d	6.26
3	0.03	s	0.67
		p	0.86
		d	6.50
4	0.04	s	0.67
		p	0.89
		d	6.48

below the Fermi level. We also observe that *d waves* contribute most to the surface states. So in this context the d waves are responsible for the sharp feature observed in the Fe(OO1) spectra. However, the d waves do no extend significantly into the vacuum region as is suggested by Ref. [1].

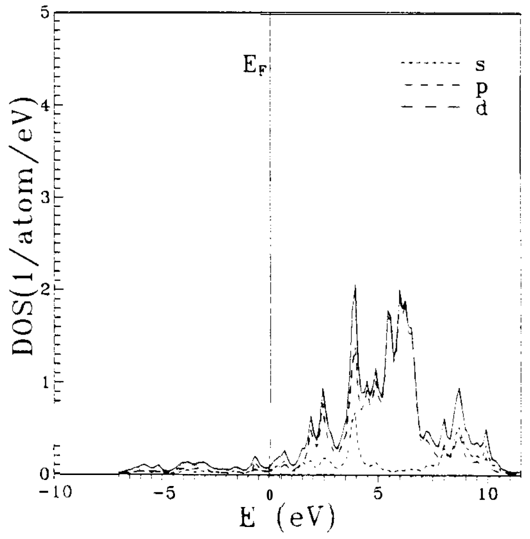

FIG. 1. Local density of states of the empty layer.

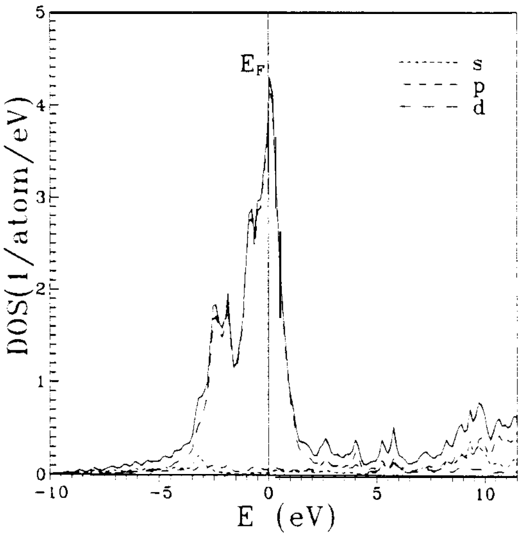

FIG. 2. Local density of states of Fe in the surface layer.

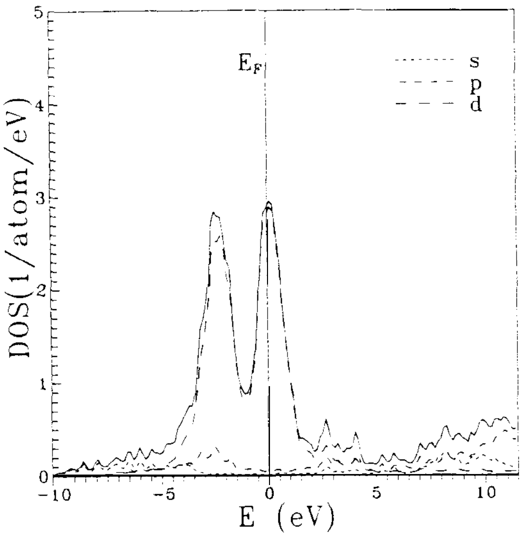

FIG. 3. Local density of states of Fe in the layer below the surface.

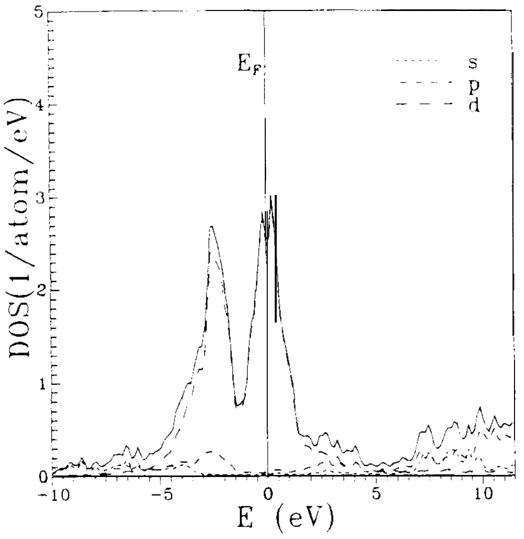

FIG. 4. Local density of states of Fe in the 2nd layer below the surface

Since the calculation is based on first principles, it inevitably has to include a few approximations to streamline the process and to make the computation manageable. The discrepancies between the calculation and experiments may come from the local density approximation, the atomic sphere approximation, and the exclusion off orbitals [14]. But its overall performance is quite satisfactory.

In summary, this *ab initio* calculation successfully connects the surface states of Fe(001) above and below the Fermi level to the experiments. It also shows that the *d* waves are responsible for these states. The method is straightforward and efficient and has the advantage of working in real space. It should be an effective tool in predicting and explaining the surface electronic structure and should see more applications in low symmetry surface systems.

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