

Prediction of Surface States of V(OO1) and Mn(OO1)

Chih-Kai Yang¹, Yi-Chen Cheng², and Shi-Yu Wu³

¹Physics Group, Department of General Studies, Chang Gung College of Medicine and Technology, Kueishan, Taiwan 333, R.O.C.

²Department of Physics, National Taiwan University, Taipei, Taiwan 106, R.O.C.

³Department of Physics, University of Louisville, Louisville, KY 40292, USA

(Received February 4, 1997)

The surface states of V(OO1) and Mn(OO1) are calculated using real-space recursive Green's function and self-consistent tight-binding linear muffin-tin orbitals. The local density of states of each system indicates both the common features and the possible surface states near the Fermi level that are expected to be observed by the scanning tunneling microscope and other experimental techniques. The method can serve to complement the experimental identification of chemical species on various surfaces.

PACS. 71.15.-m - Methods of electronic structure calculations.

PACS. 71.20.Be - Transition metals and alloys.

PACS. 73.20.At - Surface states, band structure, electron density of states

I. Introduction

The surface states of metals have recently attracted special attention owing to the introduction of the scanning tunneling microscope (STM) into their investigations [1-3]. The STM registers different resonance tunneling conductance for different chemical species on the surface. Accordingly, this technique can be applied to chemical identification of surfaces, crystal growth, and the research of alloys. Since the resonance tunneling conductance is proportional to the electronic density of states (DOS), a calculation of the electronic structure of surface system is supposed to bring out the same information as the STM experiment has to offer.

In this article we will present an *abinitio* calculation of the electronic structure of the (001) surface systems of vanadium and manganese. We have previously applied the method to Cr(001) and Fe(OO1) [4-5] and obtained results in good agreement with existing experiments. This calculation should serve as a prediction of future experimental work.

The calculation is formulated using Green's function in real space [6]. A real-space method can be more easily applied to low symmetry systems. So the calculation is suitable for a broad range of surface problems. The Green's function $G(z)$ is defined as

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

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,

$$D(E) = -\frac{1}{\pi} \lim_{\epsilon \rightarrow 0} \text{Tr} \text{Im} G(E + i\epsilon), \quad (2)$$

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

The calculation of the Hamiltonian makes use of the tight-binding linear muffin-tin orbitals (LMTO) [7-9]. The Hamiltonian also undergoes the Löwdin orthogonalization. The general formulation can be found from Ref. 6 as well as Ref. 9. The major difference that sets the calculation apart from that of Ref. 6 is in the structure matrix. The screened structure matrix \bar{S} can be separately calculated before it is joined with the physical part of the system to yield the Hamiltonian. \bar{S} is derived by the equation [9],

$$\bar{S} = S(I - \bar{Q}S)^{-1}, \quad (3)$$

where I is the unit matrix, \bar{Q} a diagonal matrix which makes the range of orbitals the shortest, and S the unscreened structure matrix. The calculation of S includes all the atomic spheres so that the surface characteristics are incorporated into the calculation at the earliest stage. For the structure of bcc (001) systems, 15 layers of atoms and one layer of empty spheres are assembled. Each of the 15 layers consists of 25 atoms. The empty layer is, of course, prepared for the extension of charge distribution out of the surface. Since the second neighbor interaction is not important in the calculation, including more empty layers in the system would not affect the surface DOS significantly. All matrix inversions are carried out by a set of recursive equations [10-11], which make the computation manageable and more efficient. Finally, the self-consistent procedures use the technique of scaling[8] to turn out a new set of parameters that are better adapted to the real physical system, allowing also the exchange of charges among the layers. Generally, after three rounds of the calculation of DOS the parameters converge and self-consistency is attained.

Figs. 1(a) and 1(b) display the DOS of the surface layers of V and Mn respectively. Their corresponding bulk DOS are shown in Figs. 2(a) and 2(b), each representing the third layer below the surface. The two bulk DOS show the general features of the electronic structure of transition metals. The energy levels are split by crystal field and are characterized by the E and T_2 symmetry. The Fermi level shifts between the peaks of DOS according to the number of valence electrons. At the surface, the reduced coordination further splits energy levels, producing peaks of DOS near the Fermi level.

The exchange of charges between atomic spheres of different layers are largely confined within the outer three layers, which include the empty overlayer. The extension of wave function outside the surface creates a negatively charged overlayer. The accumulated charges are 0.78e per atomic sphere for V and 0.73e for Mn, as shown in Tables I and II. The extended wave function is constituted mostly by s and p waves, which tend to be loosely bound. Not surprisingly, the surface layer provides the charge transferred elsewhere, leaving itself positively charged. The losses of electrons are 1.03e for V, and 0.88e for Mn. Apparently some charges move to layers below the surface. But except for the immediate layer below the surface, none receives or gives up significant amount of charges. This in a sense limits the surface effect to only a few top layers.

Fig. 1(a) shows there is one peak of DOS 0.12 eV below the Fermi level of the surface layer of V(001), which should be detected by the STM. There are two more peaks located at 1.1 eV, and 1.8 eV respectively. They probably could not be observed under small bias

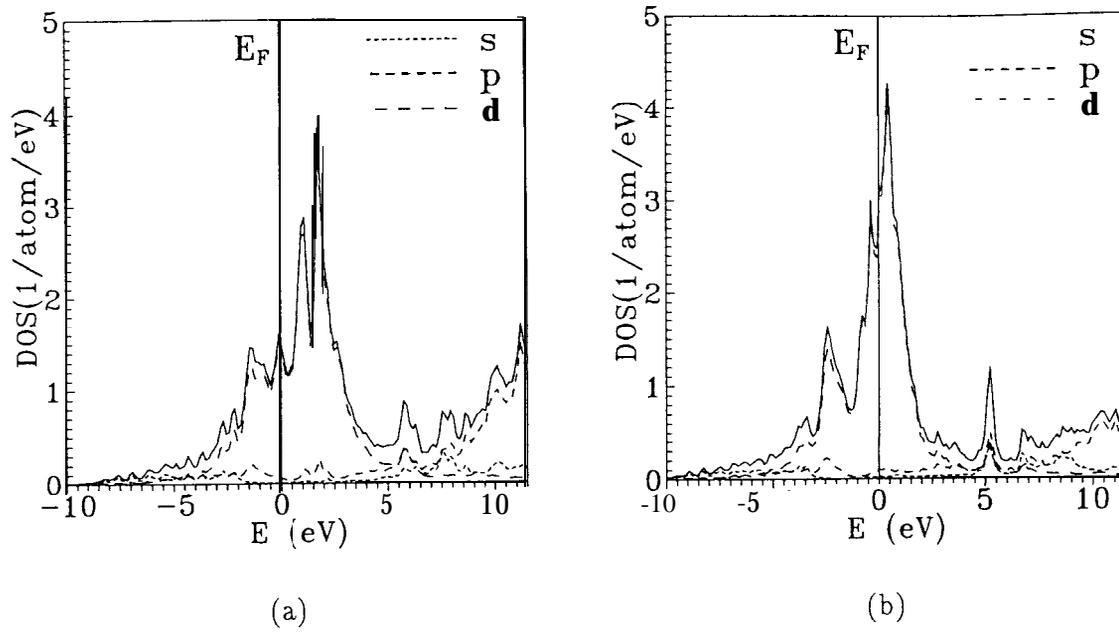


FIG. 1. (a) Local density of states of the surface layer of V(OO1). (b) Local density of states of the surface layer of Mn(OO1).

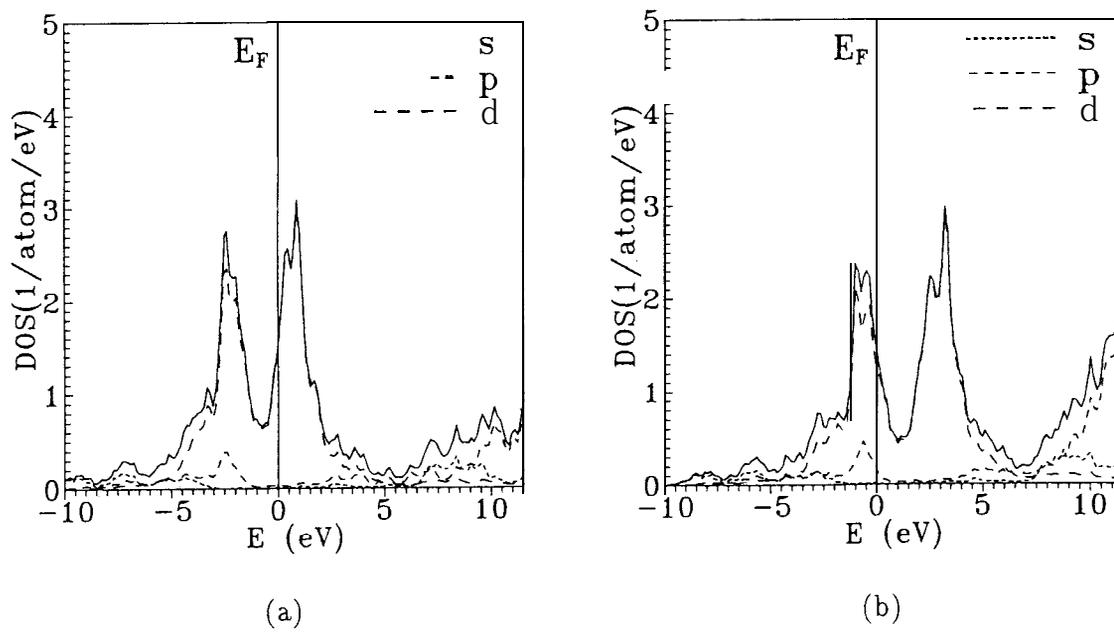


FIG. 2. (a) Local density of states of V in the 3rd layer below the surface. (b) Local density of states of Mn in the 3rd layer below the surface.

TABLE I. Charge transfer among the top five layers of V(OO1).

| Layer | Total charge transfer | Contributions from partial waves | |
|-------|-----------------------|----------------------------------|------|
| 1 | 0.78 | s | 0.52 |
| | | p | 0.18 |
| | | d | 0.08 |
| 2 | -1.03 | p | 0.53 |
| | | d | 0.59 |
| | | | 2.85 |
| 3 | 0.24 | p | 0.63 |
| | | d | 0.87 |
| | | | 3.74 |
| 4 | 0.06 | s | 0.64 |
| | | p | 0.90 |
| | | d | 3.52 |
| 5 | -0.03 | s | 0.64 |
| | | p | 0.89 |
| | | d | 3.44 |

voltage. The three sharp rises in DOS occur within an energy range corresponding to the trough of the bulk DOS. They are likely surface states.

Fig. 1(b) shows the DOS of the surface layer of Mn(OO1). There are two peaks close to the Fermi level of Mn(OO1). The one above the Fermi level is at 0.37 eV, that below it -0.50 eV. The two states are likely to be observed in STM tunneling spectra. There is one more sharp rise in DOS in Fig. 1(b). It is located at -2.6 eV and is unlikely to appear in the spectra. By comparing the surface DOS to the bulk DOS, we can identify the peak at -0.50 eV as a possible surface state.

Possible discrepancies between the calculation and experiment could come from the approximations adopted by the formulation. The local density approximation and the atomic sphere approximation would be the main sources of errors. And the actual structure of Mn, which is not exactly bcc, may influence the positions of surface states to some degree. However, the approximations offer relatively simple formulation and efficient computation and appear to provide reasonable results, judging from the calculation of Cr(OO1) and Fe(OO1).

In conclusion, this *ab initio* calculation produces the electronic structures of V(OO1) and Mn(OO1). Suggestions of possible surface states are made, based on the calculated local DOS. Investigations by the STM and other experimental and theoretical methods can further clarify the validity of these predictions. The calculation, as is presented, should be

TABLE II. Charge transfer among the top five layers of Mn(OO1).

| Layer | Total charge transfer | Contributions from partial waves | |
|-------|-----------------------|----------------------------------|------|
| 1 | 0.73 | s | 0.44 |
| | | p | 0.19 |
| | | d | 0.09 |
| 2 | -0.88 | s | 0.56 |
| | | p | 0.59 |
| | | d | 4.97 |
| 3 | 0.12 | s | 0.65 |
| | | p | 0.93 |
| | | d | 5.53 |
| 4 | 0.06 | p | 0.67 |
| | | d | 0.96 |
| | | | 5.44 |
| 5 | -0.03 | s | 0.67 |
| | | p | 0.95 |
| | | d | 5.36 |

a useful tool in the identification of chemical species on surfaces and other related research of surface properties.

This work was supported by the National Science Council of the Republic of China and the National Science Foundation of the United States under Contract Nos. NSC 86-2112-M-182-002-Y and OSR-9452895 respectively. It was also facilitated by the Center for High-Performance Computing of ROC.

References

- [1] J. A. Stroscio, D. T. Pierce, A. Davies, R. J. Celotta, and M. Weinert, *Phys. Rev. Lett.* **75**, 2960 (1995).
- [2] See, for instance, *Scanning Tunneling Microscopy* (Methods of Experimental Physics, Vol. **27**), eds. Stroscio and W. J. Kaiser (Academic, NY, 1993).
- [3] T. Jung, Y. W. Mo, and F. J. Himpsel, *Phys. Rev. Lett.* **74**, 1641 (1995).
- [4] C. K. Yang, *J. Phys. Soc. Jpn.*, **66**, 200 (1997).
- [5] C. K. Yang, Y. C. Cheng, and S. Y. Wu, *Chin. J. Phys.*, **35**, 90 (1997).
- [6] C. K. Yang, Y. C. Cheng, K. S. Dy, and S. Y. Wu, *Phys. Rev.* **B52**, 10803 (1995).
- [7] O. K. Andersen, *Phys. Rev.* **B12**, 3060 (1975).
- [8] H. L. Skriver, *The LMTO Method* (Springer, Berlin, 1984).

- [9] O. K. Andersen, O. Jepsen, and D. Glötzel, in *Highlights of Condensed Matter Theory*, eds. F. Bassani, F. Fumi, and M. P. Tosi (North Holland, NY, 1985).
- [10] K. S. Dy, S. Y. Wu, and T. Spratlin, *Phys. Rev. B*20, 4237 (1979).
- [11] S. Y. Wu, J. A. Cocks, and C. S. Jayanthi, *Comp. Phys. Commun.* 71, 125 (1992).