PHYSICAL REVIEW B VOLUME 52, NUMBER 15 15 OCTOBER 1995-I

Self-consistent method for the calculation of surface electronic structure and its application to Cu(110)

Chih-Kai Yang
Physics Group, Department of General Studies, Chang Gung College of Medicine and Technology, Kueishan, Taiwan 333, Republic of China

Yi-Chen Cheng
Department of Physics, National Taiwan University, Taipei, Taiwan, Republic of China

Kian S. Dy
Department of Physics & Astronomy, University of North Carolina, Chapel Hill, North Carolina 27599-3255

Shi-Yu Wu
Department of Physics, University of Louisville, Louisville, Kentucky 40292

(Received 16 January 1995; revised manuscript received 24 April 1995)

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 methods and can achieve self-consistency efficiently. As an application, the local density of states of Cu(110) atoms is calculated. The charge transfer between layers close to the surface is presented. We also derive the work function, which is in good agreement with experimental values.

I. INTRODUCTION

In this paper, we present an *ab initio* method for the self-consistent calculation of surface electronic structure. The method is based on the tight-binding linear muffin-tin orbitals (TB-LMTO) theory and the calculation of the electronic states is carried out in real space using the recursive Green's-function method. The method is capable of dealing with various types of surfaces such as thin-film surfaces, semi-infinite surfaces, step surfaces, etc. In this paper, we choose the semi-infinite perfect Cu(110) surface as a benchmark for demonstrating the applicability of this method. The perfect surface can be studied more efficiently with a two-dimensional **k**-space method. Since the eigenstates of the perfect surface are extended in two dimensions, this case study should provide a stringent test for the efficiency of the real-space method proposed.

Although there have been numerous publications devoted to the calculation of metal surface electronic structure, our approach has major advantages in that it is a real-space method, it is self-consistent (in the local density approximation), and it can efficiently deal with large imperfect surfaces. As can be found from Refs. 1–6, most surface calculations are performed by using the repeated slabs techniques. This approach is suitable for thin films but may not adequately represent a semi-infinite system, which has only one surface and becomes more bulklike a few layers inward from the surface. Recently, Bormet, Wenzien, and Scheffler[7] developed a Koringa-Kohn-Rostoker (KKR) Green-function method for semi-infinite crystal and used it to study the adsorption of atoms on Al(111) surface. Skriver and Rosengaard also employed a LMTO Green's-function method to study surface energy and work function[23,24] systematically and obtained very accurate results. Our real-space method, however, can treat both the semi-infinite and thin films efficiently. In fact it can also be applied to systems with less symmetry such as the stepped surface.[8] For the Cu(110) surface, which has received less attention in the past, we not only self-consistently calculate the local density of states (DOS) of atoms on the surface and below but also obtain the charge transfer extending out of the surface. As we shall see, this extension of charge is related to the work function.

II. RECURSIVE GREEN'S FUNCTION AND LMTO

The calculation uses the tight-binding LMTO with the atomic-sphere approximation (TB-LMTO-ASA). The details of the theory are described by Skriver[9] and Andersen, Jepsen, and Glötzel.[10] The method is found to work quite well with metallic systems and can be extended to a full potential method[11] for more complicated systems such as alloys and semiconductors. The method is based on the density-functional theory[12] with local-density approximation. The effective one-electron potential includes the usual Hartree term, electron-ion interaction, exchange-correlation potential, and Madelung term. The Madelung term is needed because there will be charge transfer between muffin-tin spheres, and it is crucial in the surface self-consistent procedure. The fundamental principles outlined above are very much the same as what Skriver and Rosengaard used in their calculations for surface properties.[23,24] The major difference arises when we apply them in real space instead of **k** space.

We use the bulk potential parameters as input for the surface calculation. The basis set includes the *s*, *p*, and *d* orbitals. The *f* orbitals are excluded to make the Hamiltonian matrix smaller and to save computing resources. Being a real-space method, the Hamiltonian matrix is

0163-1829/95/52(15)/10803(4)/$06.00

built layer to layer. The layer is in turn constructed out of chains of atoms. The exact geometry depends on the nature of the system and its symmetry. The matrix elements of the Hamiltonian are calculated with screened linear muffin-tin orbitals and with their overlap terms.[10] The Green's function $G(z)$ is defined 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:

$$D(E)=-\frac{1}{\pi}\lim_{\epsilon\to 0}\operatorname{Tr}\operatorname{Im}G(E+i\epsilon)\ , \tag{2}$$

where Tr and Im denote the trace of the imaginary part of $G(E+i\epsilon)$. To avoid direct inversion of matrix, which for very large systems could take up large memory space and even overwhelm the computing facility, we apply the recursive equations[13,14] to handle the job. 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

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

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

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

where

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

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

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

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

Thus, using this recursive set of equations, we can perform our calculation using small matrices while enlarging the system until it includes the whole system or until it converges for the case of an infinite system. The recursive Green's-function method has been used in many contexts such as the layer KKR method used in low-energy electron diffraction theory[15] as well as the iterative tight-binding procedures worked out by Cyrot-Lackmann[16] and Haydock, Heine, and Kelly.[17] We found the procedure outlined above to be the most efficient one because of the following: (1) It provides a framework for a systematic, real-space, local approach to the study of complex systems with low symmetry. (2) It is easily adapted to stable numerical computation. (3) At a given stage of its development, it includes all the information concerning all the degrees of freedom enclosed within that step. Thus, if the convergence of a system property is reached, the result will represent the system property without any confusion. (4) It leads to a direct determination of the eigenfunction in terms of the local basis functions, thus providing a convenient way to include the self-consistent procedure in the calculation if one is desired. The detail discussion can be found in Wu, Cocks, and Jayanthi.[18]

III. THE CALCULATION OF THE Cu(110) SURFACE

One of our goals in the example is to obtain the charge distribution on the Cu(110) surface. To allow the electron to occupy the space outside the Cu surface, we added two layers of empty spheres to the surface. In Fig. 1 we show the two empty overlayers to the surface, each with the same geometrical arrangements as the corresponding fcc layers inside. We expect the electrons moving in the overlayers to be much like free electrons and their initial potential parameters to be similar to the empty spheres in other applications.[19]

As stated in Sec. II, how many layers are enough to ensure the system is semi-infinite depends upon whether the layers we are interested in could achieve reasonable convergence. We found that using up to 22 layers, the local DOS of the tenth layer below the surface has converged toward the bulk DOS. Each of the 22 layers consists of 20 Cu atoms and a two-dimensional periodic boundary condition is imposed in each layer. The entire system consists of 440 atomic spheres, which is a large system when self-consistent calculations are involved. As a matter of fact, the calculation of Madelung potential suggests that starting from the sixth layer inward the atoms are essentially bulklike. The Madelung potential appears because each layer with excess charge is affecting the other charged layers. In order to simplify the calculation we only include the monopole term. It is calculated with Ewald's method[20] converted to meet the two-dimensional requirements. This conversion does not produce an exact analytical form and must be calculated numerically. The

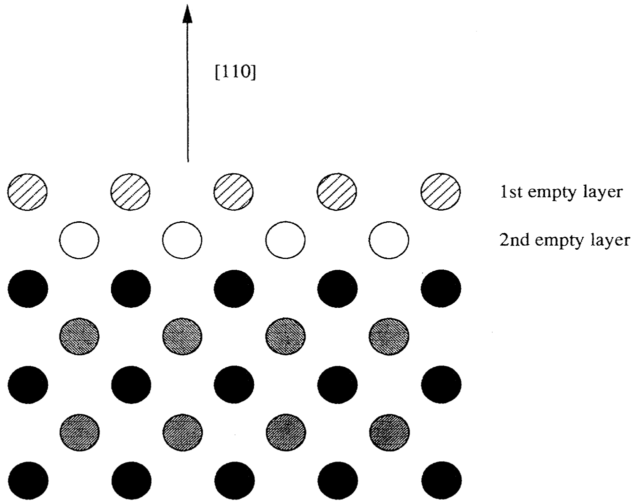

FIG. 1. Two empty layers over the Cu(110) perfect surface. Darker and lighter circles represent atoms in two different planes with mutual distance $a/2$, where a is the lattice constant.

two empty layers are included in the self-consistent calculation in the following way. One Cu atom or one empty sphere from each layer is taken out to form a neutral cell. Within the cell charges flow between the atoms in a way dictated by the self-consistent potential. The output parameters from such a limited procedure are then taken as the new input for another round of DOS calculation. Finally the self-consistency is considered attained when the potential parameters no longer have significant variations.

From Figs. 2(a)–2(f) the DOS of the top six layers, counting from the outermost empty layer inward, are shown. In all the figures the Fermi energy is placed at the zero of the energy scale. Table I gives the charge transfer per atom of the six layers. It is interesting to note the outer empty layer has a charge of 0.45*e* per muffin-tin sphere and the inner empty layer has a higher value of 0.60*e*. The DOS distribution of the first layer is also narrower than the second one. The *s* and *p* waves contribute the most states in empty spheres, with only a small portion (less than 12%) from *d* waves. This is of course in agreement with the fact that the *s* and *p* waves in Cu are more loosely bound to Cu and are therefore more likely to extend above the Cu surface. The *d* waves are so localized that they are virtually confined to the Cu atom. When compared layer by layer, the surface Cu atoms have the largest share of contribution with 0.32*e* per atom, while the other layers release less than 0.1*e* per atom. One also observes the DOS of Cu is getting more bulklike from Fig. 2(c) to Fig. 2(f).

Our definition of work function is the minimum energy required to move one electron from the surface Cu to occupy the state of the empty sphere above the Fermi energy. We obtain the value of 4.1 eV for the outer empty layer and 4.2 eV for the inner layer, in good agreement with experimental data. Gartland, Berge, and

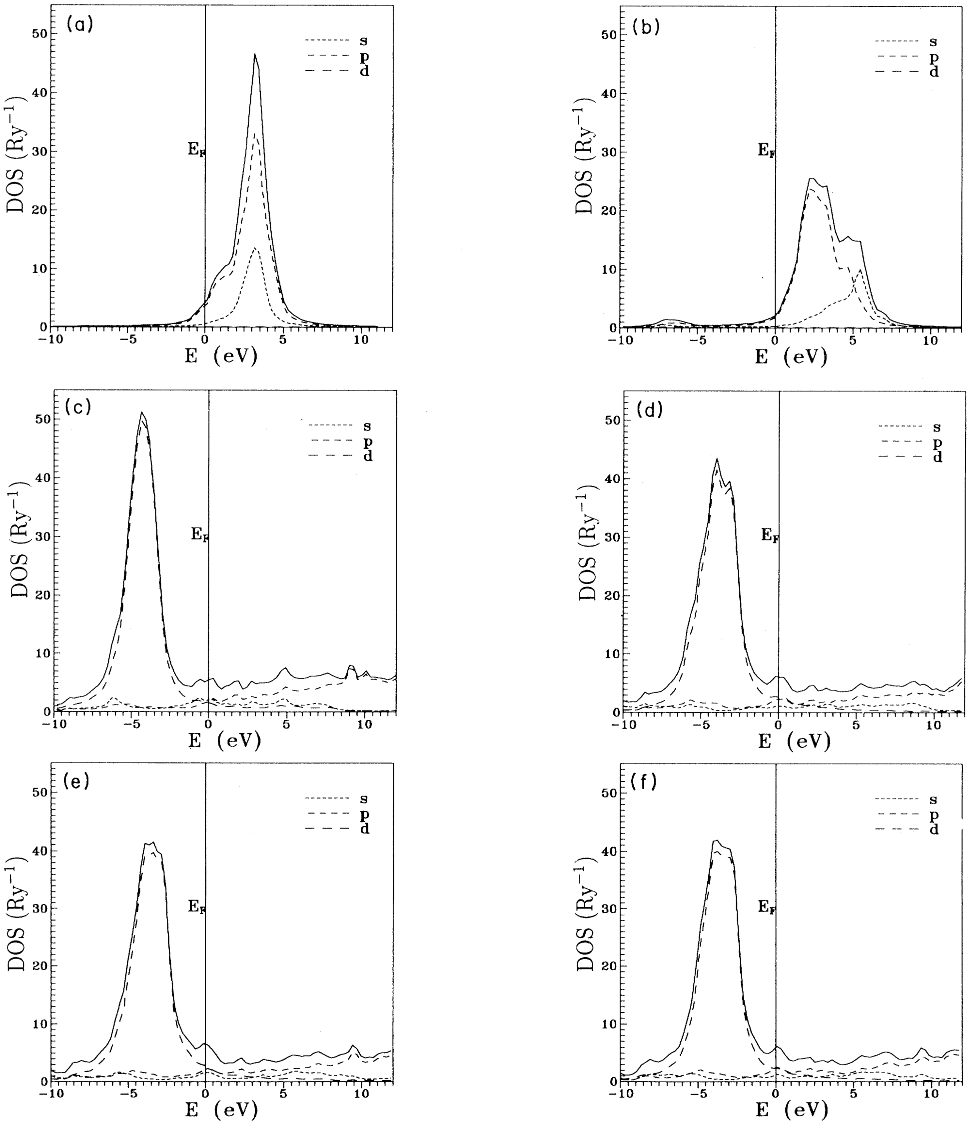

FIG. 2. Local density of states of (a) the outer empty layer, (b) the inner empty layer, (c) Cu in the surface layer, (d) Cu in the layer below the surface, (e) Cu in the second layer below the surface, and (f) Cu in the third layer below the surface.

TABLE I. Charge transfer between the six layers shown from Fig. 2(a) to Fig. 2(f).

Layer	Total charge transfer	Orbitals	
1	0.45	*s*	0.08
		p	0.32
		d	0.05
2	0.60	*s*	0.15
		p	0.38
		d	0.07
3	−0.32	*s*	−0.21
		p	0.58
		d	−0.69
4	−0.06	*s*	−0.25
		p	0.84
		d	−0.65
5	−0.09	*s*	−0.27
		p	0.84
		d	−0.66
6	−0.08	*s*	−0.25
		p	0.84
		d	−0.67

Slagsvold,[21] for example, reported 4.48 eV for the (110) face of a Cu single crystal. A value of 4.4 eV was provided by Hass and Thomas.[22] Many factors could be responsible for the discrepancy between the calculation and experiment besides the local-density-approximation. One is the omission of the dipole contribution in the Madelung potential.[23–26] Another is the use of the smaller basis set that does not include the *f* orbitals, according to Crampin.[26] Despite these possible sources of errors our calculated work function seems surprisingly good. The major reason could be that the work function is derived directly from the local DOS, which may not be very sensitive to those factors. Also pointed out by Szunyogh *et al.*,[27] the number of vacuum layers has negligible effects on the DOS. So our choice of two empty layers, which makes the matrices smaller, is expected to derive reasonable work function from the DOS.

IV. CONCLUSIONS

We develop an *ab initio* method for the calculation of surface electronic structure. The real-space approach is efficient and is expected to be applied to complex systems such as stepped surfaces and surface adsorptions. In fact, we have found it suitable for stepped surface[8] and are currently developing a fully self-consistent scheme for that purpose.

The particular example of our self-consistent calculation of semi-infinite Cu(110) surface shows that charges make their way into the region outside the surface. A dipole layer is thus formed by the negatively charged layers outside the surface and the positive layers inside. The derived work function is close to experimental values. However, future development of the method could be directed to study the effects of what we have ignored in the calculation to further improve the accuracy.

ACKNOWLEDGMENTS

This work was supported by the National Science Council of the Republic of China under Contract No. NSC 83-0208-M-182-004 and was facilitated by the nation's Center for High-Performance Computing. One of us (S.Y.W.) would like to acknowledge the support of the National Science Foundation (USA) through (i) Grant No. EHR-9108764 and (ii) Grant No. OSR-9452895.

---

[1] C.-Q. Ma, M. V. Ramana, and B. R. Copper, Phys. Rev. B **34**, 3854 (1986).

[2] A. Euceda, D. M. Bylander, L. Kleinman, and K. Mednick, Phys. Rev. B **27**, 659 (1983).

[3] J. R. Smith, J. G. Gay, and F. J. Arlinghaus, Phys. Rev. B **21**, 2201 (1980).

[4] J. A. Appelbaum and D. R. Hamann, Solid State Commun. **27**, 881 (1978).

[5] D. G. Dempsey and L. Kleinman, Phys. Rev. B **16**, 5356 (1977).

[6] M. Heinrichsmeier and A. Fleszar, Surf. Sci. **285**, 129 (1993).

[7] J. Bormet, B. Wenzien, and Matthias Scheffler, Comput. Phys. Commun. **79**, 124 (1994).

[8] C. K. Yang, Y. C. Cheng, and S. Y. Wu, Phys. Lett. A **188**, 68 (1994).

[9] H. L. Skriver, *The LMTO Method* (Springer, Berlin, 1984).

[10] O. K. Andersen, O. Jepsen, and D. Glötzel, in *Highlights of Condensed Matter Theory,* edited by F. Bassani, F. Fumi, and M. P. Tosi (North-Holland, New York, 1985).

[11] P. P. Singh and A. Gonis (unpublished).

[12] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn and L. J. Sham, *ibid.* **140**, A1133 (1965).

[13] K. S. Dy, S. Y. Wu, and T. Spratlin, Phys. Rev. B **20**, 4237 (1979).

[14] S. Y. Wu, J. A. Cocks, and C. S. Jayanthi, Comput. Phys. Commun. **71**, 125 (1992).

[15] J. M. MacLaren, S. Crampin, and D. D. Vvedensky, Phys. Rev. B **40**, 12 176 (1989); J. M. MacLaren, S. Crampin, D. D. Vvedensky, and J. B. Pendry, *ibid.* **40**, 12 164 (1989).

[16] For example, F. Cyrot-Lackmann, Adv. Phys. **16**, 393 (1967); J. Phys. Chem. Solids **29**, 1235 (1968); Surf. Sci. **15**, 535 (1969).

[17] R. Haydock, V. Heine, and M. J. Kelly, J. Phys. C **5**, 2845 (1972).

[18] S. Y. Wu, J. A. Cocks, and C. S. Jayanthi, Phys. Rev. B **49**, 7957 (1994).

[19] For example, C. K. Yang and K. S. Dy, Solid State Commun. **88**, 491 (1993).

[20] J. M. Ziman, *Principles of the Theory of Solids* (Cambridge University Press, Cambridge, England, 1964).

[21] P. O. Gartland, S. Berge, and B. J. Slagsvold, Phys. Rev. Lett. **28**, 738 (1972).

[22] G. A. Hass and R. E. Thomas, J. Appl. Phys. **48**, 86 (1977).

[23] H. L. Skriver and N. M. Rosengaard, Phys. Rev. B **43**, 9538 (1991).

[24] H. L. Skriver and N. M. Rosengaard, Phys. Rev. B **46**, 7157 (1992).

[25] S. Crampin, J. Phys. Condens. Matter. **5**, 4647 (1993).

[26] S. Crampin, Phys. Rev. B **49**, 14 035 (1994).

[27] L. Szunyogh, B. Ujfalussy, P. Weinberger, and J. Kollár, Phys. Rev. B **49**, 2721 (1994).