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1992 J. Phys.: Condens. Matter 4 1047

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## Electron correlation on metallic surfaces

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Received 5 July 1991

**Abstract.** Electron correlation on metallic surfaces is studied for the first time with the use of the slave-boson functional integral method. The ground-state properties of the semi-infinite simple-cubic model in the non-magnetic state are investigated. The double occupancy,  $\delta_n$ , and the band narrowing factor,  $q_n$ , on layer  $n$  are calculated as a function of the electron interaction. It is shown that  $\delta_1$  and  $q_1$  on the surface show a peculiar behaviour depending on the ratio  $U_1/U_b$  where  $U_1$  ( $U_b$ ) denotes the interaction on the surface (in the bulk).

### 1. Introduction

The study of electron correlation has been one of the most interesting subjects in solid-state physics. The effect of electron correlation in the Hubbard model has been investigated by using various approaches (Gutzwiller 1963, Hubbard 1964, Kanamori 1963). Quite recently, Kotliar and Ruckenstein (KR) (1986) proposed the slave-boson functional integral method which has various advantages. The simplest saddle-point approximation to the KR method leads to the Gutzwiller approximation (Gutzwiller 1963). The KR method can be applied not only to the ferromagnetic state but also to the antiferromagnetic state (Kotliar and Ruckenstein 1986, Hasegawa, 1989a, b, 1990a). It yields very accurate results when compared with exact results obtained by Monte Carlo simulations (Yokoyama and Shiba 1987a, b, Lilly *et al* 1990). Fluctuations around the saddle-point solution in the KR method lead to a result consistent with that obtained in the random phase approximation (Rasul and Li 1988, Li *et al* 1989). The effect of electron correlation at finite temperatures is discussed by combining the KR method with the alloy-analogy approximation (Hasegawa 1989a, 1990a). Thus, the KR method is a promising and useful approach to the study of electron correlation, and has a wide applicability.

During the last decade there has been considerable progress in our theoretical understanding of surface properties, particularly of transition metals (for a review see Freeman *et al* 1985). The electronic structures of transition-metal surfaces have been calculated by using the first-principles local density functional (LDF) method or by using the realistic tight-binding model. These approaches have been very successful in explaining not only bulk properties but also surface properties. In these methods, however, the many-body effect is not properly taken into account, though the LSD method includes it in the form of a suitably averaged one-electron exchange-correlation potential. One of the examples showing the importance of its effect is the fact that the d-band width of *bulk* Ni observed by the photoemission experiment

is reduced by 25% compared to the value calculated with the LDF method (Himpsel *et al* 1979). This kind of many-body effect is expected to be more significant in the calculations of surface bands than in those of the bulk, because the effect of electron correlation on the surface is greater than in the bulk. It is desirable to include the many-body effect more correctly in the band calculation of the surface. It is the purpose of the present paper to study the effect of electron correlation on a metallic surface by using the KR method. This is the first step going beyond the conventional approximations. As will be shown shortly, electron correlation on a metallic surface is much more involved than that in the bulk.

The paper is organized as follows. In the next section we describe an application of the KR method to the surface-related subject. A numerical calculation is presented in section 3, where the effect of electron correlation in the non-magnetic semi-infinite simple-cubic model is discussed. A summary and supplementary discussions are given in the final section.

## 2. Formulation

We adopt the semi-infinite simple-cubic model with a (001) surface (Hasegawa 1990b). The layers parallel to the surface are assigned by the index  $n$ , which is 1 for the top surface layer. The system is described by the Hubbard Hamiltonian given by

$$H = \sum_{\sigma} \sum_i E_i c_{i\sigma}^{\dagger} c_{i\sigma} + \sum_{\sigma} \sum_{i,j} t_{ij} c_{i\sigma}^{\dagger} c_{j\sigma} + \sum_i U_i n_{i\uparrow} n_{i\downarrow} \quad (1)$$

where  $c_{i\sigma}^{\dagger}$  ( $c_{i\sigma}$ ) is a creation (annihilation) operator of a  $\sigma$ -spin electron on the lattice site  $i$ , and  $n_{i\sigma} = c_{i\sigma}^{\dagger} c_{i\sigma}$ . The core potential,  $E_i$ , and the electron-electron interaction,  $U_i$ , are assumed to be  $E_n$  and  $U_n$ , respectively, if the site  $i$  belongs to the  $n$ th layer. The hopping integrals,  $t_{ij}$ , are assumed to vanish when the site  $i$  or  $j$  is located outside the surface.

The model Hamiltonian given by (1) was used by many authors to investigate surface properties within the Hartree-Fock approximation (Takayama *et al* 1974, Weling 1980). We will take into account the effect of electron correlation, which has been neglected so far, by using the KR functional integral method. Since an application of the KR method to the surface problem goes almost parallel to that of the bulk case, we briefly describe it. Kotliar and Ruckenstein (1986) introduced four boson fields which act as projection operators onto the empty, singly occupied sites with spin  $\sigma$  ( $=\uparrow$  and  $\downarrow$ ), and doubly occupied states at a given site. By performing the functional integral in terms of the boson fields and employing a change of variables (Kotliar and Ruckenstein 1986, Hasegawa 1989a), we get a partition function given by

$$Z = \int D\xi Dm D\nu Dn D\delta \exp(-\beta S) \quad (2)$$

with

$$\exp(-\beta S) = \exp\left[-\beta \sum_i (U_i \delta_i + \xi_i m_i - \nu_i n_i)\right] \text{Tr} \exp\left(-\beta \sum_{\sigma} H_{\sigma}\right) \quad (3)$$

$$H_{\sigma} = \sum_i (E_i + \nu_i - \sigma \xi_i) c_{i\sigma}^{\dagger} c_{i\sigma} + \sum_{ij} (q_{i\sigma} q_{j\sigma})^{1/2} t_{ij} c_{i\sigma}^{\dagger} c_{j\sigma} \quad (4)$$

where  $Dm = \Pi_i m_i$  etc,  $m_i$  is the magnetic moment,  $n_i$  the number of electrons,  $\xi_i$  the exchange field,  $\nu_i$  the charge field and  $\delta_i$  is the double occupancy at site  $i$ . The effective Hamiltonian for a  $\sigma$ -spin electron,  $H_\sigma$ , shows that the hopping integral,  $t_{ij}$ , is reduced by a factor  $(q_{i\sigma}q_{j\sigma})^{1/2}$ , where  $q_{i\sigma}$  is the band-narrowing factor given by

$$q_{i\sigma} = 2\{[(n_i + \sigma m_i - 2\delta_i)(1 - n_i + \delta_i)]^{1/2} + [\delta_i(n_i - \sigma m_i - 2\delta_i)]^{1/2}\}^2 \times [(n_i + \sigma m_i)(2 - n_i - \sigma m_i)]^{-1}. \quad (5)$$

The total energy is thus given by

$$E = \sum_n \left( (U_n \delta_n + \xi_n m_n - \nu_n n_n) + \int d\epsilon f(\epsilon) \epsilon \sum_\sigma \rho_{n\sigma}(\epsilon) \right) \quad (6)$$

where  $\delta_n$ ,  $\xi_n$ ,  $\nu_n$ ,  $m_n$ , and  $n_n$  are expectation values on the layer  $n$  determined by the following simultaneous equations (Hasegawa 1989a):

$$U_n + \sum_\sigma (\partial q_{n\sigma} / \partial \delta_n) R_{n\sigma} = 0 \quad (7)$$

$$2\xi_n / \tilde{J}_n = m_n = \int d\epsilon f(\epsilon) \sum_\sigma \sigma \rho_{n\sigma}(\epsilon) \quad (8)$$

$$2\nu_n / \tilde{U}_n = n_n = \int d\epsilon f(\epsilon) \sum_\sigma \rho_{n\sigma}(\epsilon) \quad (9)$$

with

$$\tilde{U}_n = (2U_n / n_n) \left[ \sum_\sigma (-\partial q_{n\sigma} / \partial n_n) R_{n\sigma} \right] \left[ \sum_\sigma (\partial q_{n\sigma} / \partial \delta_n) R_{n\sigma} \right]^{-1} \quad (10)$$

$$\tilde{J}_n = (2U_n / m_n) \left[ \sum_\sigma (\partial q_{n\sigma} / \partial m_n) R_{n\sigma} \right] \left[ \sum_\sigma (\partial q_{n\sigma} / \partial \delta_n) R_{n\sigma} \right]^{-1} \quad (11)$$

$$R_{n\sigma} = \int d\epsilon f(\epsilon) [(\epsilon - \nu_n + \sigma \xi_n) / q_{n\sigma}] \rho_{n\sigma}(\epsilon) \quad (12)$$

$$\rho_{n\sigma}(\epsilon) = (-1/\pi) \text{Im} F_{n\sigma}(z) |_{z=\epsilon+i0} \quad (13)$$

$$F_{n\sigma}(z) = \langle i | (z - H_\sigma)^{-1} | i \rangle \quad i \in n. \quad (14)$$

Here  $f(\epsilon)$  is the Fermi distribution function, and  $\tilde{U}$  and  $\tilde{J}$  are effective Coulomb and exchange interactions, respectively. We allow the expectation values of  $X_n$  ( $= \delta_n$  etc) on the first  $N$  layers to be different from  $X_b$  ( $= \delta_b$  etc) in the bulk, by imposing the following boundary conditions:  $X_n = X_b$  at  $n = N + 1$ . Bulk and surface quantities are hereafter expressed by the subscript b and s, respectively. The site-diagonal Green function,  $F_{n\sigma}(z)$ , is evaluated by using the transfer-matrix method (Falicov and Yudurain 1975).

### 3. Calculated results

We consider the non-magnetic ground state of the half-filled simple-cubic model with nearest-neighbour hopping. For the bulk the double occupancy,  $\delta_b$ , and the band narrowing factor,  $q_b$ , are simply given by (Gutzwiller 1963, Brinkman and Rice 1970)

$$4\delta_b = 1 - U_b/U_{bc} \quad q_b = 8\delta_b(1 - 2\delta_b) = 1 - (U_b/U_{bc})^2 \quad (15)$$

where  $U_{bc} = 8|E_{b0}|$ ,  $E_{b0}$  being the ground-state energy of the bulk with  $U = 0$ .

As for  $\delta_n$  and  $q_n$  for arbitrary  $n$ , we solved the self-consistent equations given by (5)–(14), assuming the configuration with  $N = 2$ . The surface core potential,  $E_1$ , was adjusted to preserve local charge neutrality. The interactions were chosen as  $U_b = U_2 = U$  and  $U_1 = \alpha U$ . For a given  $\alpha$  value, we performed calculations by changing  $U$ .

Figures 1(a) and (b) show  $\delta_n$  and  $q_n$  against the layer index,  $n$ , for various  $U$ , which is measured in units of a half width of the bulk band for  $U = 0$ . Results for  $n = 1$ ,  $n = 2$  and  $n \geq 3$  denote those for the surface, sublayer and bulk, respectively. Full (broken) curves show the results for  $\alpha = 1.0$  ( $\alpha = 0.8$ ). In the case of  $\alpha = 1.0$ , calculated  $\delta_n$  and  $q_n$  on the surface are always smaller than those in the bulk, while results for the sublayer are almost the same as those in the bulk. This means that the effect of electron correlation on the surface is more significant than in the bulk. In the case of  $\alpha = 0.8$ ,  $\delta_1$  and  $q_1$  become larger than those in the bulk because of the weakened surface interaction.

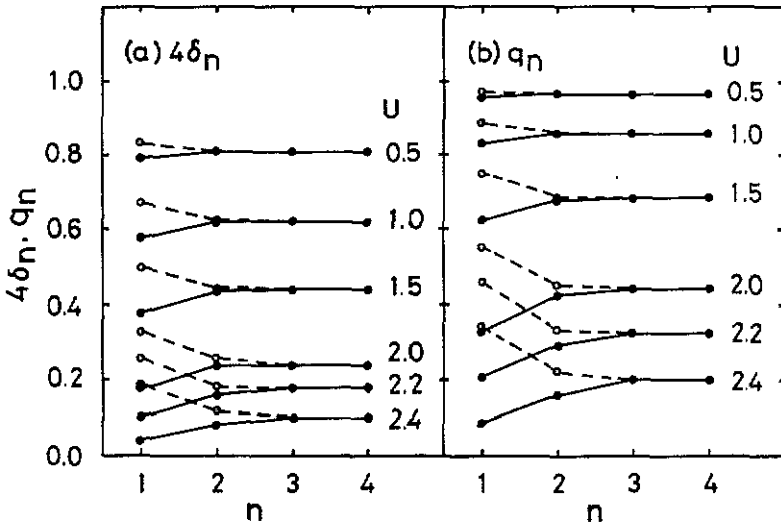


Figure 1. Profiles of (a) the double occupancy,  $\delta_n$ , and (b) the band narrowing factor,  $q_n$ , for various  $U$  values for  $\alpha = 1.0$  (full curves) and  $\alpha = 0.8$  (broken curves).

The  $U$  dependences of the double occupancy and the band narrowing factor for  $\alpha = 1.2, 1.0, 0.8$  and  $0.6$  are shown in figures 2(a)–(d). Broken curves show results for the bulk, which is given analytically by (15). We note that  $\delta_b$  and  $q_b$  vanish when  $U$  exceeds  $U_{bc}$ , which is a critical interaction for the metal–insulator transition (Brinkman and Rice 1970). Full curves show the results for the surface, exhibiting a peculiar behaviour.

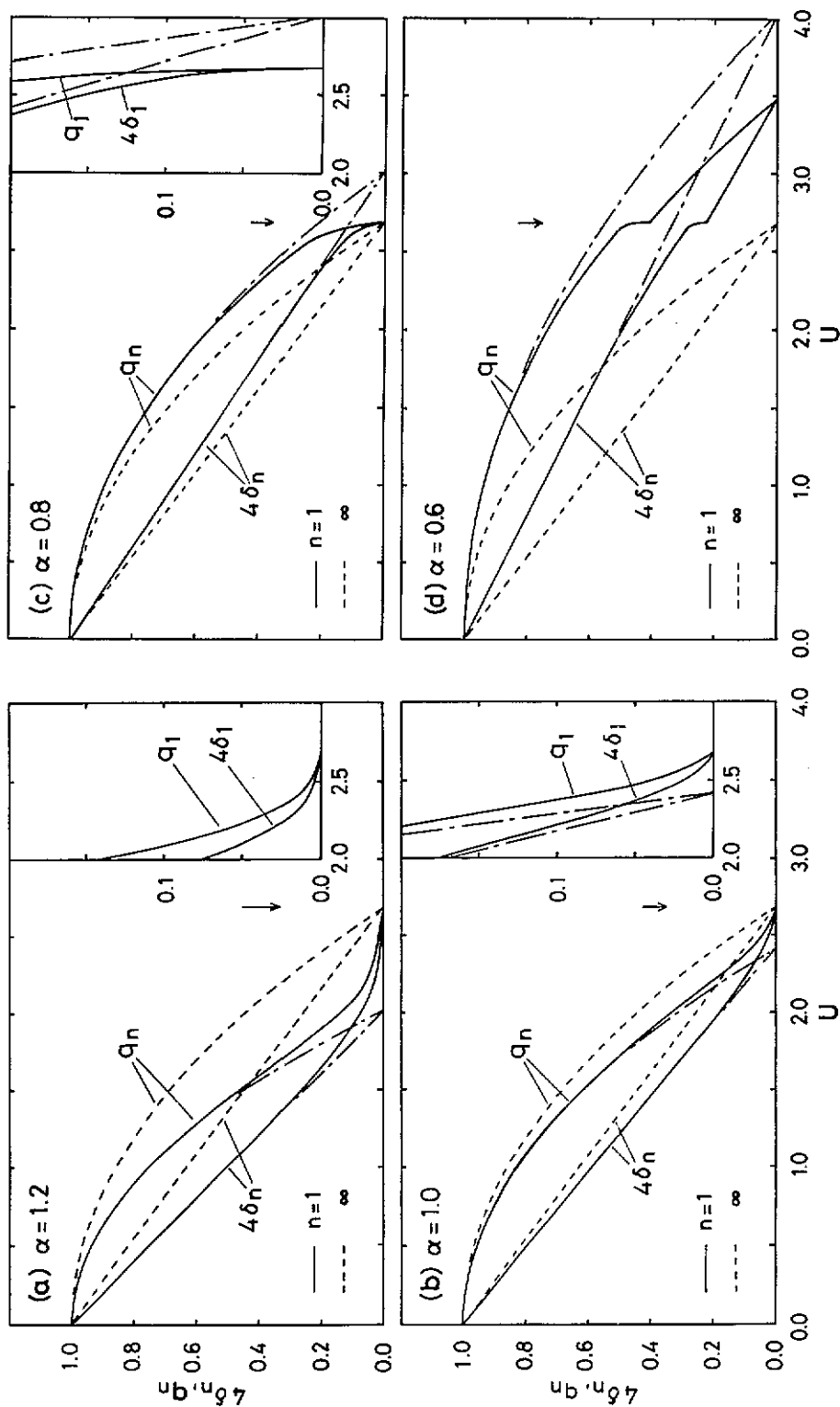


Figure 2. The  $U$  dependence of the double occupancy,  $\delta_n$ , and the band-narrowing factor,  $q_n$ , on the surface ( $n = 1$ ; full curves) and in the bulk ( $n = \infty$ ; broken curves) for (a)  $\alpha = 1.2$ , (b) 1.0, (c) 0.8 and (d) 0.6. Broken and chain curves denote equations (15) and (16), respectively. The arrow expresses the critical interaction,  $U_{bc}$ , above which  $\delta_b$  and  $q_b$  vanish. The insets show enlarged figures for  $U \sim U_{bc}$ .

First we consider the case of  $\alpha = 1.0$ , which means  $U_b = U_1 = U$ . Figure 2(b) shows that, when the interaction is small,  $\delta_1$  and  $q_1$  follow chain curves given by

$$4\delta_1 = 1 - (\alpha U/U_{s0}) \quad q_1 = 1 - (\alpha U/U_{s0})^2 \quad (16)$$

which vanish at a characteristic interaction,  $\alpha U = U_{s0}$ , defined by  $U_{s0} = 8|E_{s0}|$ ,  $E_{s0}$  being the surface contribution to the total energy for  $U = 0$ . When  $\alpha U$  approaches  $U_{s0}$ ,  $\delta_1$  and  $q_1$  have a different  $U$  dependence, remaining finite at  $\alpha U = U_{s0}$ . They gradually decrease at  $U_{s0}/\alpha < U < U_{bc}$  and vanish at  $U \geq U_{bc}$ . Usually  $U_{s0}$  is smaller than  $U_{bc}$  (our model leads to  $U_{s0} = 2.420$  and  $U_{bc} = 2.679$ ), since the surface density of states for  $U = 0$  is narrower than the bulk density of states because of missing bonds on the surface. The  $U$  dependence of  $\delta_1$  and  $q_1$  shows a crossover when  $\alpha U$  approaches and exceeds  $U_{s0}$ .

In the case of  $\alpha = 0.8$ , the  $U$  dependence of  $\delta_1$  and  $q_1$  exhibits a different behaviour, as shown in figure 2(c). When  $\alpha U \ll U_{s0}$ ,  $\delta_1$  and  $q_1$  follow chain curves, as in the case of  $\alpha = 1.0$ . When  $U$  approaches  $U_{bc}$ , however, they show a new  $(1 - U/U_{bc})^{1/2}$  dependence near  $U_{bc}$  and vanish at  $U > U_{bc}$ . Thus the behaviour of  $\delta_1$  and  $q_1$  near  $U_{bc}$  for  $\alpha = 0.8$  is different from that for  $\alpha = 1.0$ . We found that this transition occurs at a critical value of  $\alpha_0$  defined by  $\alpha_0 = E_{s0}/E_{b0}$  ( $= 0.903$  in our model). When  $\alpha = \alpha_0$ , the  $U$  dependence of  $\delta_n$  and  $q_n$  for all  $n$  almost obey expressions similar to (15) or (16).

When  $\alpha$  is further decreased to be less than the critical value of  $\alpha_c = U_{fc}/U_{bc}$  ( $= 0.78$  in our model),  $\delta_1$  and  $q_1$  are found to show an interesting behaviour: the surface may be metallic on an insulating substrate (bulk). Here  $U_{fc} = 8|E_{f0}|$  is the characteristic interaction relevant to the metal-insulator transition of the  $N$ -layer film which is effectively isolated from the insulating substrate (bulk),  $E_{f0}$  being its non-interacting energy. The result for  $\alpha = 0.6$  is shown in figure 2(d). We note that the metallic state on the surface actually persists even at  $U > U_{bc}$  where

$$4\delta_1 = 1 - (\alpha U/U_{fc}) \quad q_1 = 1 - (\alpha U/U_{fc})^2 \quad (17)$$

while the bulk is insulating ( $\delta_b = q_b = 0$ ).

We expect from physical considerations that, when  $U_1 = \alpha U > U_{s0}$  and  $U_b = U < U_{bc}$ , the surface may become an insulator on metallic surfaces ( $\delta_1 = 0, \delta_b \neq 0$ ). We found, however, that this is not realized in our calculation. A numerical example for  $\alpha = 1.2$  is plotted in figure 2(a). In the region of  $U_{s0}/\alpha < U < U_{bc}$ ,  $\delta_1$  and  $q_1$  become very small, though they remain finite. This is because the surface density of states is broadened by electron hopping from the metallic substrate (bulk).

Similar calculations have been performed by changing  $\alpha$  and  $U$ . Figures 3(a) and (b) show the calculated phase diagram in the  $U$ - $\alpha$  and  $U_b$ - $U_1$  planes, respectively. The numerical calculations reported above were performed along thin lines in figure 3(b) denoting  $U_1 = \alpha U_b$  with  $\alpha = 0.6$ -1.2. We have the three phases, A, B and C. In the A phase both the surface and the bulk are metallic ( $\delta_1 \neq 0, \delta_b \neq 0$ ), and in the C phase they are both insulators ( $\delta_1 = 0, \delta_b = 0$ ). However, in the B phase the surface is metallic but the bulk is an insulator ( $\delta_1 \neq 0, \delta_b = 0$ ). The B and C phases are separated from the A phase by the line  $U_b = U = U_{bc}$ . The boundary between the B and C phases is given by  $U_1 = \alpha U = U_{fc}$ . In a part of the A phase above the dotted curve denoting  $U_1 = \alpha U = U_{s0}$ ,  $\delta_1$  and  $q_1$  are finite but fairly small.

The densities of states on the surface, sublayer and bulk for the three cases are shown in figures 4(a)-(c). In the case of (a)  $U = 0$ , the band narrowing factors

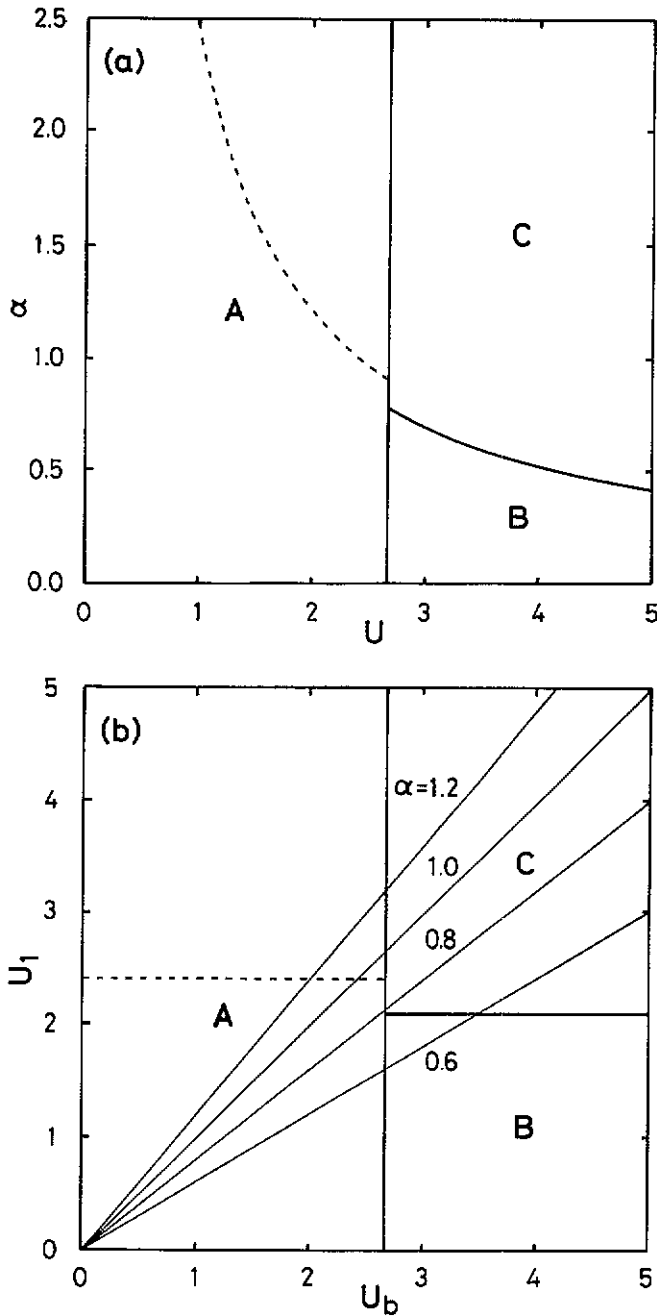
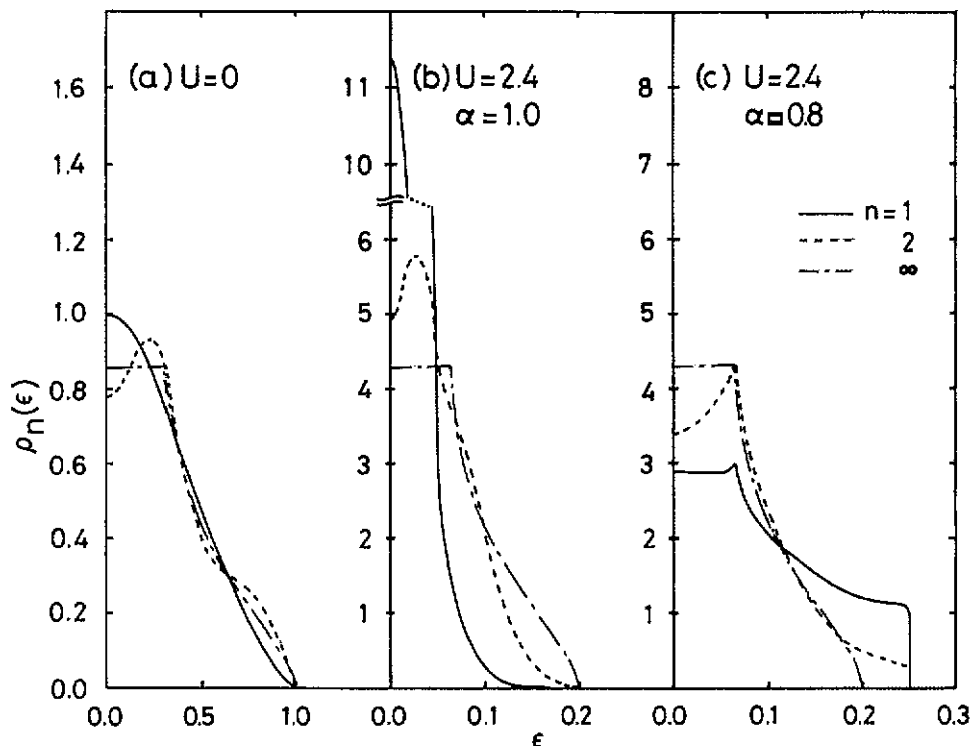


Figure 3. The phase diagram of the non-magnetic half-filled band in (a) the  $U$ - $\alpha$  plane and (b) the  $U_b$ - $U_1$  plane. The three phases, A, B and C, are characterized by A ( $\delta_1 \neq 0, \delta_b \neq 0$ ), B ( $\delta_1 \neq 0, \delta_b = 0$ ) and C ( $\delta_1 = 0, \delta_b = 0$ ). The dotted curve expresses  $U_1 = \alpha U = U_{s0}$ , above which  $\delta_1$  and  $q_1$  are finite but very small (see text). Thin full curves denote  $U_1 = \alpha U_b$  with fixed  $\alpha$  values.

are  $q_1 = q_2 = q_b = 1.0$ , and the densities of states are the same as those obtained previously (Kalkstein and Soven 1971). In the case of (b)  $U = 2.4$  and  $\alpha = 1.0$ , we



obtain  $q_1 = 0.086$ ,  $q_2 = 0.159$  and  $q_b = 0.198$ . The surface has narrower and higher densities of states than the bulk because  $q_1 < q_b$ . In the case of (c)  $U = 2.4$  and  $\alpha = 0.8$ , we get  $q_1 = 0.343$ ,  $q_2 = 0.226$  and  $q_b = 0.198$ , which yields the surface band wider than the bulk. Cusps at  $\epsilon = 0.067$  in the densities of states on the surface and sublayer arise from the Van Hove singularity. The step-like structure in their band edges is due to the two-dimensional character of the adlayers.



**Figure 4.** Densities of states,  $\rho_n(\epsilon)$ , on the surface layer ( $n = 1$ ; full curves), sublayer ( $n = 2$ ; broken curves) and in the bulk ( $n = \infty$ ; chain curves) for (a)  $U = 0.0$ , (b)  $U = 2.4$  ( $\alpha = 1.0$ ) and (c)  $U = 2.4$  ( $\alpha = 0.8$ ). The density of states is symmetric about its centre. Note that horizontal and vertical scales for (b) and (c) are different from those for (a).

#### 4. Summary

We have discussed the effect of electron correlations on metallic surfaces by using the KR method (Kotliar and Ruckenstein 1986). Our calculation has demonstrated that electron correlation on the surface shows much more variety than that in the bulk. Although we adopted a simple system with  $N = 2$  in the model calculation, our essential conclusion would not be modified for systems with larger  $N$ . We note that the behaviour of  $\delta_1$  and  $q_1$  on the surface depends on the ratio  $\alpha = U_1/U_b$ . This situation is similar to the molecular-field theory of the Heisenberg model for free surfaces (Binder 1983), in which surface magnetization and its critical exponent depend on the ratio of  $J_s/J_b$ ,  $J_s(J_b)$  being the exchange interaction on the surface (in

the bulk). In the present calculation, we changed  $U$  for a given value of  $\alpha = U_1/U_b$ . We may allow the surface potential,  $E_1$ , and surface hopping integrals,  $t_1$ , to be different from those in the bulk. These add more variety to the study of electron correlation on metallic surfaces.

It is well known that the half-filled band favours the antiferromagnetic state more than the non-magnetic one. Monte Carlo simulations (Kaplan *et al* 1982, Yokoyama and Shiba 1987b) and analytical calculations (Hasegawa 1989a) for the bulk show that when the antiferromagnetism is taken into account, neither  $\delta_b$  nor  $q_b$  vanish as long as  $U$  is finite. This is also expected to be the case in our calculation if antiferromagnetism is included: both  $\delta_1$  and  $\delta_b$  remain finite as long as  $U_b$  and  $U_1$  are finite. One of the interesting effects of electron correlation is that it works to suppress long-range order on the surface and in the bulk. Although calculated magnetic moments on Fe, Ni and Cr surfaces are reported to be much enhanced compared with the bulk (Freeman *et al* 1985), it is possible that surface moments may be reduced from the calculated values if we take into account the effect of the electron correlation, which is neglected in the conventional band calculations. Calculations of surface moments including the effect of electron correlation are in progress, and will be reported elsewhere.

### Acknowledgments

This work was started while the author was in Tohoku Gakuin University, Sendai. It was partly supported by a Grant-in-Aid for Scientific Research on Priority Areas from the Japanese Ministry of Education, Science and Culture.

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