

## Calculation of the electronic work function of Cu and Ag from an extended jellium model

V. Russier\* and J. P. Badiali

*Structure et Réactivité aux Interfaces Université Pierre et Marie Curie,  
4 place Jussieu, 75230 Paris CEDEX 05, France*

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We propose an extended jellium model which includes the most important features of the noble metals. The density of states is modeled by the superposition of a  $d$  band and an  $s$ -like conduction band. The redistribution of some of the  $d$  electrons into the conduction band as an effect of the  $s$ - $d$  hybridization is taken into account, and the conduction band includes 1.5 electrons per atom. We show that the occupation number  $Z_d$  of the  $d$  band is mainly determined by the ratio  $W_d/(\epsilon_F - \epsilon_d)$ , where  $W_d$ ,  $\epsilon_d$ , and  $\epsilon_F$  are, respectively, the width and the center of the  $d$  band and the energy of the Fermi level. The shift of the  $d$ -band center between the bulk metal and the surface plane is related to the narrowing of the  $d$  band of the surface plane, and we deduce an estimate of the  $d$ -band contribution to the work function. In the present model the position of the Fermi level and of the  $d$ -band center are reproduced, and the result for the work function of Cu and Ag is satisfactory.

### I. INTRODUCTION

For simple metals, the surface properties which result from an average along the surface (surface energy, work function, etc.) can be calculated in the framework of the simple jelliumlike model with satisfactory accuracy.<sup>1-5</sup> These models are constructed in the spirit of both the pure jellium model and simple-metal pseudopotential theory.<sup>6</sup> Thus two important simplifications are made: on one hand, the model is one dimensional; on the other hand, the effect of the ionic lattice is represented by a weak pseudopotential. Therefore, in this kind of approach one deals with the problem of an electron gas immersed in an external field. Moreover, owing to the properties of the density-functional theory,<sup>7,8</sup> some approximate treatments based on variational principles<sup>9,10</sup> can be used. In the case of pure jellium for some of the most important surface properties (surface energy, work function, and position of the static image plane), such variational calculations lead to results very close to the "exact" numerical ones.<sup>11</sup>

For the noble metals (Cu, Ag and Au) the jelliumlike models are not sufficient to obtain reliable results for the surface properties, in particular for the work function. Indeed, although the experimental work function of noble metals is not established with certainty, the values calculated by Lang and Kohn<sup>2</sup> for Cu, Ag, and Au are undoubtedly too small by about 1 eV. This discrepancy is not unexpected since in the work of Lang and Kohn the presence of the  $d$  band is totally ignored while this is one important physical feature of the noble metals. After the treatment of Lang and Kohn, the work function of noble metals has been calculated from *ab initio* methods.<sup>12,13</sup> Until the present time, however, no simple model which includes the peculiarities of these metals has been proposed.

In this work we consider a simple one-dimensional model, constructed in the spirit of the jellium model, which takes into account, at least qualitatively, the peculiarities of the noble metals. As an application we focus on the calculation of the work function. To this aim we start from the first-principles formalism developed by Moriarity<sup>14,15</sup> for the bulk metal, in order to examine what physical features are the most important for the work function. Particular attention is paid to the density of states of the bulk metal from which one can define the occupation numbers  $Z_d$  and  $Z_s$  of the  $d$  band and the pure  $s$  band in the metal. This is important since it has been found, from different approaches,<sup>16,17</sup> that  $Z_s$  differs significantly from the nominal valence of the free atom for both Cu and Ag ( $Z_s \simeq 1.5$ ). We find that the work function includes two important contributions which can be calculated separately in a first approximation. The first one is the work function of an "effective simple metal" characterized mainly by  $Z_s$ . The second contribution is the potential drop due to the narrowing of the  $d$  band in the surface crystallographic plane. In the present work the  $d$ -band contribution, which is the smallest contribution, is calculated by a very approximate version of the tight-binding method.

The paper is organized as follows. In Sec. II we examine the density of states of the bulk metal and we separate the total density of states into an  $s$ -band part and a  $d$ -band part. In Sec. III we next examine the different contributions to the work function and then calculate the  $d$ -band and "effective-simple-metal" contributions. The results are given and discussed in Sec. IV.

### II. DENSITY OF STATES IN THE BULK

In simple metals the electronic states can be separated into ionic-core states and conduction-band states. This

separation, the small-core approximation, which is the starting point of the usual pseudopotential theory,<sup>6</sup> is due to the fact that the energy levels of the ionic-core states lie well below the bottom of the conduction band. As a result the eigenstates corresponding to the free atom remain good eigenstates for the total Hamiltonian in the metal. Then, when one deals with simple metals one can treat these two kinds of electrons separately, and a large number of properties can be accounted for by considering only a nearly-free-electron gas immersed in the ionic lattice, represented by a weak pseudopotential (see, for instance, the works concerning the surface properties of simple metals.<sup>1-5</sup>).

In the case of transition and noble metals, such a separation is not possible because of the presence of the  $d$  electrons whose energy states coincide with the conduction band. As a result, besides the inner-core states for which the small-core approximation is still valid, one has to consider on an equal footing the  $d$ , and the conduction, electrons. The pseudopotential theory has been extended to the case of noble metals by Harrison<sup>18</sup> and extensively developed by Moriarty,<sup>14-16,19,20</sup> leading to the generalized pseudopotential theory (GPT). However, although a parametrized version of the GPT has been introduced<sup>21</sup> in order to make the formalism more tractable, the GPT method involves heavy computations even in the bulk. Thus our aim is not to extend the GPT to the surface problem, but to construct a simple model for the calculation of the work function of Cu and Ag. In this section we use the results of the treatment of Moriarty<sup>14-16,19,20</sup> for the bulk noble metals in order to get a simple treatment without losing the most important physical features for the work function.

The formalism developed by Moriarty is based on a perturbation scheme where two perturbative operators are used. The first one is the nonlocal pseudopotential  $W$ ,

$$W = (1 - P_c)V, \quad (2.1)$$

where  $V$  is the total potential in the metal and  $P_c$  is the inner-core-state projection operator,

$$P_c = \sum_c |c\rangle \langle c|. \quad (2.2)$$

This pseudopotential is weak for the nearly-free-electron states, but is strong for the  $d$  electrons because of the  $l=2$  resonance. Then the  $d$  states in the metal are expanded in a basis set including both plane waves  $|\mathbf{k}\rangle$  and localized, reference  $d$  states  $|d\rangle$ . These reference  $d$  states are not, in general, those of the free atom but rather those of closely related "zero-order pseudoatoms," which are constructed in order to optimize the expansion.<sup>16</sup> Thus in the pseudoatoms the  $d$  states are intermediate between the  $d$  states in the free atom and the actual  $d$  states in the metal. Then one defines the difference  $\delta V$  between the potential in the metal  $V$  and the potential in the pseudoatom  $V_{pa}$ ,

$$\delta V = V_{pa} - V, \quad (2.3)$$

and the second perturbative operator of the formalism is

given by

$$\Delta = \delta V - \langle d | \delta V | d \rangle. \quad (2.4)$$

This operator is effectively weak for the  $d$  states since it only becomes strong well outside the ionic cores where the  $d$  states are small.<sup>15,16</sup> The final step in the definition of the perturbative operators is to isolate the contribution  $\delta V^{\text{vol}}$  of the potential  $\delta V$  which does not depend on the ionic structure of the metal. Then the structure-independent term of the matrix element  $\Delta_{kd} = \langle \mathbf{k} | \Delta | d \rangle$  is isolated in the form

$$\Delta_{kd} = \Delta_{kd}^{\text{vol}} + \Delta_{kd}^{\text{struct}}, \quad (2.5)$$

and here only  $\Delta_{kd}^{\text{vol}}$ , which is the dominant term, is taken into account.

In the remainder of this section we focus on the density of states (DOS) per atom  $\rho(\epsilon)$ . From the work of Moriarty<sup>14,16,19,20</sup> we know that  $\rho(\epsilon)$  can be split into four contributions:

$$\rho(\epsilon) = \rho_0(\epsilon) + \delta\rho_{sp}(\epsilon) + \rho_d(\epsilon) + \delta\rho_d(\epsilon). \quad (2.6)$$

The first one is the free-electron density of states

$$\rho_0(\epsilon) = (2^{1/2} \Omega_0 / \pi^2) (\epsilon)^{1/2}, \quad (2.7)$$

where  $\Omega_0$  is the atomic volume and  $\epsilon=0$  corresponds to the bottom of the conduction band. The second term in (2.6) is a small correction due to the pseudopotential  $W$  acting on plane waves  $|\mathbf{k}\rangle$ . When a local approximation is used for  $W$ ,<sup>6</sup> this term can be integrated in  $\rho_0$  with simply a shift,  $\langle 0 | W | 0 \rangle$ , in the origin of the energies.  $\rho_d(\epsilon)$  is the one-ion  $d$  state component of  $\rho(\epsilon)$ . From the Green-function formalism one finds<sup>14,16,19,20</sup>

$$\rho_d(\epsilon) = -\frac{10}{\pi} \text{Im} \left[ \frac{d}{dE} \ln [E - \epsilon_d - \Gamma_{dd}(E)] \right], \quad (2.8)$$

where  $E$  stands for  $\epsilon + i0^+$ .  $\epsilon_d$  is the mean, structure-independent,  $d$ -state energy in the metal and is given by

$$\epsilon_d = \epsilon_d^{\text{pa}} - \langle d | \delta V^{\text{vol}} | d \rangle, \quad (2.9)$$

where  $\epsilon_d^{\text{pa}}$  is the  $d$ -state energy in the zero-order pseudoatom and  $\delta V^{\text{vol}}$  is the structure-independent part of  $\delta V$ .<sup>16</sup>  $\Gamma_{dd}(E)$  is the  $d$ -state self-energy which can be written in the form, for  $\epsilon$  near  $\epsilon_d$  [i.e., replacing  $\Delta^{\text{vol}} + (\epsilon - \epsilon_d)$  by  $\Delta^{\text{vol}}$ ]

$$\Gamma_{dd}(E) = \frac{2\Omega_0}{(2\pi)^3} \int \langle \mathbf{k} | \Delta^{\text{vol}} | d \rangle \langle d | \Delta^{\text{vol}} | \mathbf{k} \rangle \frac{d\mathbf{k}}{E - k^2/2}. \quad (2.10)$$

The last term in (2.6) is a correction to  $\rho_d$  which takes into account the structural effects of the DOS. Concerning the DOS itself,  $\delta\rho_d$  is important since it describes the broadening and the structure of the  $d$  band. However,  $\delta\rho_d$  is oscillatory in nature<sup>14,16</sup> and thus its average over occupied states is small.

Now we are mainly interested in the integrated DOS  $N(\epsilon)$  given by

$$N(\epsilon) = \int_0^\epsilon \rho(\epsilon') d\epsilon', \quad (2.11)$$

from which the Fermi level can be defined according to

$$N(\epsilon_F) = Z_s + Z_d, \quad (2.12)$$

where  $Z_s$  and  $Z_d$  are the number of conduction and  $d$  electrons per atom, respectively. In Cu and Ag we have  $N(\epsilon_f) = 11$ .  $Z_s$  and  $Z_d$  can be separated, at least formally, from the different contributions of the DOS. Thus we have, by using a local approximation for  $W$ ,

$$Z_s = N_0(\epsilon_F) = \frac{\Omega_0}{3\pi^2} (2\epsilon_F)^{3/2}. \quad (2.13)$$

When a nonlocal approximation is used for the pseudopotential  $W$ , a one-ion term must be added (see Appendix C of Ref. 19). As we have already mentioned,  $\delta N_d$  corresponding to  $\delta\rho_d$  is small and accordingly we take, from (2.8),

$$\begin{aligned} Z_d &= N_d(\epsilon_F) \\ &= -\frac{10}{\pi} \text{Im} \{ \ln [E_F - \epsilon_d - \Gamma_{dd}(E_F)] \}. \end{aligned} \quad (2.14)$$

When the zeroth-order pseudoatoms are chosen in such a way that Eqs. (2.12)–(2.14) are satisfied, the zeroth-order value of  $Z_s$  is very close to the one obtained from a (LMTO) determination.<sup>17</sup>

Notice that (2.14) implies that the states corresponding to the  $d$  electrons behave beyond the Fermi level as the tail of a resonant  $d$  state immersed in a free-electron-like continuum. This conclusion was already pointed out by Terakura<sup>22</sup> from a somewhat different perspective. As a result, the  $d$ -band-like DOS is not totally filled ( $Z_d < 10$ ) even for Cu and Ag. Indeed, Moriarty obtained  $Z_d \simeq 9.5$  (and hence  $Z_s \simeq 1.5$ ) for both Cu and Ag and a similar result was obtained by Christensen and Heine<sup>17</sup> from a LMTO calculation. It is important to notice that the shift of the Fermi level due to the  $s$ - $d$  coupling<sup>19</sup> is properly reproduced by the free-electron formula (2.13) when the valence is changed from the nominal value ( $Z_s = 1$ ) to the actual value in the metal ( $Z_s \simeq 1.5$ ) and this justifies, *a posteriori*, the utilization of a local approximation for the pseudopotential  $W$ .

Now we examine what the relevant quantities which determine  $Z_s$  are. First, from (2.14) we get a more convenient expression,

$$Z_d = -\frac{10}{\pi} \arctan \left[ \frac{\Gamma''_{dd}(\epsilon_F)}{\epsilon_F - \epsilon_d - \Gamma'_{dd}(\epsilon_F)} \right], \quad (2.15)$$

where  $\Gamma'_{dd}$  and  $\Gamma''_{dd}$  are, respectively, the real and imaginary parts of  $\Gamma_{dd}$  and can be calculated by transforming Eq. (2.10). After the results of Moriarty,<sup>15,16</sup> we can check that  $\Gamma'_{dd}$  is quite small when compared to  $\epsilon_F - \epsilon_d$ , which is known from complete *ab initio* band-structure calculations.<sup>23</sup> Therefore we can drop  $\Gamma'_{dd}$  in Eq. (2.15). On the other hand,  $\Gamma''_{dd}$  can be written, for  $\epsilon$  near  $\epsilon_d$ , in the form

$$\begin{aligned} \Gamma''_{dd}(\epsilon) &= -\pi(2\epsilon)^{1/2} \\ &\times \left[ \int j_2(\sqrt{2\epsilon}r) \Delta^{\text{vol}}(r) R_2(r) dr \right]^2, \end{aligned} \quad (2.16)$$

[see Eq. (14) of Ref. 24], where  $rR_2(r)$  is the radial part of the wave function representing the reference (or pseudoatom)  $d$  state  $\Phi_{dm}$ ,

$$\Phi_{dm}(\mathbf{r}) = rR_2(r) Y_2^m(\hat{\mathbf{r}}). \quad (2.17)$$

As proposed in Refs. 25 and 26, we use the expansion of the spherical Bessel function  $j_s(kr)$  for the small values of  $k = \sqrt{2\epsilon}$  [ $j_2(kr) \simeq 2(kr)^2/15$ ] and the energy dependence of  $\Gamma''_{dd}$  can be explicitly written as

$$\Gamma''_{dd}(\epsilon) = \Gamma''_{dd}(\epsilon_F) \left[ \frac{\epsilon}{\epsilon_F} \right]^{5/2}. \quad (2.18)$$

In the case of Cu the form (2.18) reproduces nearly exactly the result of the complete calculation given in Ref. 15 and we expect a similar conclusion for Ag.

At the same time, we know that  $\Gamma'_{dd}(\epsilon_d)$  gives the width of the resonance,<sup>14,26</sup> which is related to the width of the  $d$  band.<sup>26</sup> We have the following approximation in the case of the fcc structure, which is that of Cu and Ag,

$$W_d = -\frac{225}{4} \Gamma''_{dd}(\epsilon_d) \frac{1}{r_0^5 (2\epsilon_d)^{5/2}}, \quad (2.19)$$

where  $r_0$  is the distance between next-nearest neighbors at equilibrium. Now from (2.18) and (2.19) we can express  $\Gamma''_{dd}(\epsilon_F)$  in terms of  $W_d$  and  $(\epsilon_F)^{5/2}$ . Then we use (2.13) to relate  $\epsilon_F$  to  $Z_s$  and, accordingly, we see from (2.15) that  $Z_d$  is determined only by the ratio  $W_d/(\epsilon_F - \epsilon_d)$  and this is the most important result of this section. We have

$$10 - Z_d = \frac{10}{\pi} \arctan \left[ \frac{4}{225} \left[ \frac{3\pi^2 r_0^3 Z_s}{\Omega_0} \right]^{5/3} \frac{W_d}{\epsilon_F - \epsilon_d} \right]. \quad (2.20)$$

On the other hand,  $W_d$  can also be related to the structure of the ionic lattice following the ideas of the tight-binding approach.<sup>27</sup> We have<sup>26</sup>

$$W_d = 4 \sum_i (N_i/5)^{1/2} [(dd\sigma)^2 + 2(dd\pi)^2 + 2(dd\delta)^2]^{1/2}, \quad (2.21)$$

where the sum runs over the shells of neighbors including  $N_i$  ionic sites, and the  $ddm$  ( $m = 0, \pm 1, \pm 2$ ) are the usual two-center overlap integrals.<sup>26,28–30</sup> In the following we shall consider only the first-nearest neighbors. Then the sum in (2.21) includes only one term and the corresponding  $N$  is replaced by the coordination number  $c$ .

Fortunately, as we shall see in the next section, since the  $d$  band is partially filled  $Z_d < 10$ ,  $Z_d$  appears to be a central quantity, and since  $Z_d$  is determined by the ratio  $W_d/(\epsilon_F - \epsilon_d)$  the details of the DOS are found to be unessential for the work function. Moreover, one can verify that the Fermi level is properly determined by the free-electron relation (2.13) provided the correct value of  $Z_s$  is used. Therefore, the results of the GPT concerning the density of states suggest splitting the electronic states in a nearly-free-electron band characterized by  $Z_s$  and a partially filled  $d$  band which can then be treated separate-

ly in a first approximation.

As we shall see in the next section, for the work function we do not need to specify the shape of the  $d$ -band DOS and we shall use for  $Z_s$  (or  $Z_d$ ) and  $\varepsilon_d$  the values listed in Table I. Therefore our model differs from that of Wills and Harrison,<sup>31</sup> where the rectangular model, introduced by Friedel,<sup>27</sup> is used for the  $d$ -band DOS. Indeed, with the Friedel model one obtains a partially filled  $d$  band only with an unphysical shift of  $\varepsilon_d$  towards  $\varepsilon_F$ . In fact, this problem remains even if one uses a more refined model for the  $d$  band if the  $d$  band is calculated in the framework of a pure tight-binding treatment (ignoring the  $s$ - $d$  coupling) as, for instance, the moment method.<sup>28,32</sup> We emphasize that the equation for  $Z_d$  obtained by Moriarty results from a complete treatment including the  $s$ - $d$  coupling which is responsible for the tail in the  $d$  band extending beyond the Fermi level and leading to  $Z_d < 10$  (see Ref. 17 for a discussion on this point).

### III. WORK FUNCTION

The separation of the total density of states into a nearly-free-electron-band DOS, a reference  $d$ -band DOS, and an oscillatory term which does not contribute significantly in the integrated DOS suggests a simple model for the calculation of the work function. The work function is given by

$$\Phi = -\varepsilon_F + \Delta\varphi, \quad (3.1)$$

where  $\varepsilon_F$  is the Fermi level relative to the mean electrostatic potential in the metal and  $\Delta\varphi$  is the potential drop between the vacuum and the bulk of the metal, corresponding to  $z \rightarrow -\infty$ . In the following for the electrostatic potentials we shall use the convention  $\varphi(-\infty) = 0$ . As we have already mentioned in the preceding section, the Fermi level can be determined by the free-electron DOS  $\rho_0(\varepsilon)$ , provided that the correct value of the valence in the metal  $Z_s$  is used, through Eq. (2.13).

Then we have to determine  $\Delta\varphi$ . First of all, we separate  $\Delta\varphi$  into a contribution due to the conduction electrons,  $\Delta\varphi_s$ , and a contribution due to the  $d$  electrons,  $\Delta\varphi_d$ ,

$$\Delta\varphi = \Delta\varphi_s + \Delta\varphi_d. \quad (3.2)$$

On the other hand,  $\Delta\varphi$  can be written in the form

$$\Delta\varphi = \Delta\varphi^{(0)} + \Delta\varphi^{(\Delta)}, \quad (3.3)$$

where  $\Delta\varphi^{(0)}$  is the potential drop obtained by neglecting the coupling between the conduction electrons and the reference  $d$  states which correspond to the partially filled

$d$  band. This coupling is responsible for the term  $\Delta\varphi^{(\Delta)}$ . Thus we have

$$\Delta\varphi = \Delta\varphi_s^{(0)} + \Delta\varphi_d^{(0)} + \Delta\varphi^{(\Delta)}. \quad (3.4)$$

$\Delta\varphi_s^{(0)}$  is the potential drop due to the inhomogeneity of the semi-infinite nearly-free-electron gas characterized by the valence  $Z_s$ . Since  $\varepsilon_F$  coincides with the Fermi level of the same nearly-free-electron gas, this system defines an effective simple metal (MS) which is obtained by neglecting the partially filled  $d$  band, and whose work function is given by

$$\Phi_{\text{MS}} = -\varepsilon_F + \Delta\varphi_s^{(0)}. \quad (3.5)$$

The work function of the actual metal is then

$$\Phi = \Phi_{\text{MS}} + \Delta\varphi_d^{(0)} + \Delta\varphi^{(\Delta)}. \quad (3.6)$$

$\Delta\varphi_d^{(0)}$  is the potential drop due to the  $d$  bands located on the ionic sites of the semi-infinite lattice. The calculation of  $\Delta\varphi_d^{(0)}$  involves the usual tight-binding (TB) method.<sup>28-30</sup> The remaining term is due to the coupling between the two kinds of electronic states. The calculation of this term necessitates the knowledge of the total electronic density  $n(\mathbf{r})$  at the same level of approximation as that used by Moriarty for the calculation of the bulk total electronic density  $n_b(\mathbf{r})$ .<sup>15,19</sup> However, we know from the work of Moriarty<sup>15</sup> that if the reference system used is characterized by  $Z_s = 1.5$ , the term  $\delta n$  due to the  $s$ - $d$  coupling is small. We assume that this is also the case for the inhomogeneous system and we neglect  $\Delta\varphi^{(\Delta)}$  in our calculation of the work function. We emphasize that neglecting  $\Delta\varphi^{(\Delta)}$  does not mean that the  $s$ - $d$  coupling is neglected since this coupling is taken into account through the value of the valence  $Z_s$  in the metal.

Therefore we are left with the calculation of the work function of the effective simple metal and the potential drop  $\Delta\varphi_d^{(0)}$ .

#### A. $d$ -band contribution.

In order to determine the potential drop  $\Delta\varphi_d^{(0)}$  we use the tight-binding approximation, which has been developed for some surface properties of the transition metals.<sup>28-30,32</sup> The quantity which plays a central role is the local density of states (LDOS) corresponding to the  $d$  band centered on a given ionic site labeled  $i$ . Here we consider only the case of an ideal semi-infinite ionic lattice (without any surface reconstruction or lattice relaxation) and therefore all the ions of a given lattice plane are equivalent; accordingly, the LDOS will refer to a given lattice plane rather than to a given ionic site (the surface plane will be labeled by  $i = 0$ ).

In the tight-binding approximation the  $d$  states and the two-center overlap integrals  $dd\sigma$ ,  $dd\pi$ , and  $dd\delta$  are considered to be the same in the surface plane and in the bulk. Then by taking into account only the overlap integrals corresponding to the first-nearest neighbors, an approximation justified in the case of the fcc structure which is that of the noble metals, one gets from (2.21)

$$W_d^{(0)}/W_d = (c^{(0)}/c)^{1/2}, \quad (3.7)$$

TABLE I. Bulk parameters used in the present work.  $\varepsilon_F$ : free-electron Fermi level calculated with  $Z_s$ . The energies are in eV.

	$Z_s$	$r_c$ (a.u.)	$\varepsilon_F$	$\varepsilon_F - \varepsilon_d$
Cu	1.5	0.869	9.2	2.5
Ag	1.5	0.85	7.3	4.5

where  $c^{(0)}$  and  $c$  are the coordination numbers of the ionic sites of the surface plane and of the bulk, respectively. Since  $c^{(0)}$  is smaller than  $c$ , the  $d$  band of the surface plane is narrower than in the bulk. This narrowing leads to a charge transfer between the  $d$  bands of neighboring planes near the surface and this charge transfer is responsible for the potential drop  $\Delta\varphi_d^{(0)}$ . Let  $\varphi_d(\mathbf{r})$  be the potential at the point  $\mathbf{r}$  due to the narrowing of the  $d$  band. In order to determine  $\Delta\varphi_d^{(0)}$  we only need to consider the averaged potential  $\varphi_d(z) = \langle \varphi_d(\mathbf{r}) \rangle_s$  along the surface. Thus we are left with the calculation of the electrostatic potential created by charged planes located at  $z = z_i$ . The jellium edge being located at  $z = 0$ , we have

$$z_i = -d/2 - id, \quad i \geq 0, \quad (3.8)$$

where  $d$  is the lattice plane spacing.  $Z_d$  being the occupation number of the bulk LDOS, the charge per surface unity in the  $i$ th plane is

$$q_i = -n_\Sigma(Z_d^{(i)} - Z_d) = -n_\Sigma \delta Z_d^{(i)}, \quad (3.9)$$

where  $n_\Sigma$  is the number of ions per unit of surface in the lattice planes. The electrostatic potential  $\varphi_d(z)$  is related

to the charges  $q_i$  by the Poisson equation

$$\varphi_d(z) = 4\pi \sum_i [q_i \Theta(z - z_i)(z - z_i)], \quad (3.10)$$

where  $\Theta$  is the Heaviside step function. The  $d$ -band center  $\varepsilon_d^{(i)}$  of the  $i$ th plane is shifted from that of the bulk,  $\varepsilon_d$ , mainly because of the potential  $\varphi_d(\mathbf{r})$ . We consider here, following the ideas of the tight-binding approximation, that the spatial extension of the  $|d\rangle$  states is sufficiently small for  $\varphi_d(\mathbf{r})$  to be considered a constant in the region where the  $|d\rangle$  states are nonzero; moreover, we approximate this constant,  $\varphi_d(\mathbf{r}_i)$ , by its averaged value on the surface,  $\varphi_d(z_i)$ . Secondly, the  $d$ -band center is also shifted because of the potential drop  $\varphi_s(z_i)$  due to the conduction-electron gas and we have

$$\Delta\varepsilon_d^{(i)} = \varphi_d(z_i) + \varphi_s(z_i). \quad (3.11)$$

We have shown in Sec. II that  $Z_d$  is determined to a good approximation by the ratio  $W_d/(\varepsilon_F - \varepsilon_d)$ . We assume here that from a simple generalization of Eq. (2.20)  $Z_d^{(i)}$  is determined by the ratio  $W_d^{(i)}/(\varepsilon_F - \varepsilon_d^{(i)})$ . Thus the deviation  $Z_d^{(i)} = (Z_d^{(i)} - Z_d)$  is directly related to  $\Delta\varphi_d^{(i)}$ ,

$$\delta Z_d^{(i)} = \frac{10}{\pi} \arctan \left[ \frac{4}{225} \left[ \frac{3\pi^2 r_0^3 Z_s}{\Omega_0} \right]^{5/3} \frac{W_d}{\varepsilon_F - \varepsilon_d} \right] - \frac{10}{\pi} \arctan \left[ \frac{4}{225} \left[ \frac{3\pi^2 r_0^3 Z_s}{\Omega_0} \right]^{5/3} \left[ \frac{c^{(i)}}{c} \right]^{1/2} \frac{W_d}{\varepsilon_F - \varepsilon_d^{(i)}} \right], \quad (3.12)$$

where we have used Eq. (3.7). It is easy to check that we can linearize the arctan functions given  $10 - Z_d = 0.5$ , and we have

$$\delta Z_d^{(i)} = (10 - Z_d) \left[ 1 - \frac{(c^{(i)}/c)^{1/2}}{1 - \Delta\varepsilon_d^{(i)}/(\varepsilon_F - \varepsilon_d)} \right], \quad (3.13)$$

to which we add the condition of conservation of the total number of  $d$  electrons,

$$\sum_i \delta Z_d^{(i)} = 0. \quad (3.14)$$

It is important to consider at this point the case where  $10 - Z_d = 0$ . In this case it is obvious from (3.13) that whatever the value of  $\Delta\varepsilon_d^{(i)}/(\varepsilon_F - \varepsilon_d)$  the deviation  $\delta Z_d^{(i)}$  is zero. Then the potential drop  $\Delta\varphi_d = \varphi_d(z^{(0)})$ , given by (3.10), due to the charge transfers between neighboring  $d$  bands, is zero and the shift  $\Delta\varepsilon_d^{(i)}$  is only due to the conduction electrons. This is expected since in this case  $Z_d$  cannot be increased from the bulk to the surface plane. Therefore, the  $d$  band does not contribute directly to the work function, at least in the first approximation, when  $10 - Z_d$  is zero whatever the value of the shift in the  $d$ -band center  $\Delta\varepsilon_d^{(i)}$  when going from the bulk to the surface.

When  $10 - Z_d$  is nonzero, Eqs. (3.10), (3.11), (3.13), and (3.14) form a closed set from which we can calculate the  $\Delta\varepsilon_d^{(i)}$ , and deduce  $\varphi_d^{(0)}$ .

However, as a first step we have used a pure tight-binding description where only the  $d$  band is considered,

which means that the contribution  $\varphi_s(z^{(i)})$  in (3.11) is neglected. In this case we find that  $\delta Z_d^{(0)}$  is very small ( $\sim 10^{-2}$ ), as one can see from Table II, where we give the results for both  $\delta Z_d^{(0)}$  and  $\Delta\varphi_d^{(0)}$ . Therefore,  $\Delta\varphi_d^{(0)}$  is well approximated by imposing in Eq. (3.13) the condition  $\delta Z_d^{(0)} = 0$ :

$$\Delta\varphi_d^{(0)} = [1 - (c^{(0)}/c)^{1/2}](\varepsilon_F - \varepsilon_d). \quad (3.15)$$

This result requires two remarks. On one hand, it is rather surprising to find  $\Delta\varphi_d^{(0)}$  proportional to  $\varepsilon_F - \varepsilon_d$ . However, (3.15) concerns only the case where  $10 - Z_d$  is not vanishingly small and thus  $\varepsilon_F - \varepsilon_d$  is not large. Moreover, when two different metals are characterized by the same value for  $Z_d$  and different values for  $\varepsilon_F - \varepsilon_d$ , for instance in Cu and Ag, the width of the  $d$  band follows the value of  $\varepsilon_F - \varepsilon_d$  and we expect that the importance of the  $s$ - $d$  coupling and of the  $d$  band are well estimated by the value of  $\varepsilon_F - \varepsilon_d$ . On the other hand, when  $Z_d = 0$ , for instance in Cd or Zn, the present model predicts  $\Delta\varphi_d^{(0)} = 0$  whatever the value of  $\varepsilon_F - \varepsilon_d$ .

In fact, (3.15) can be understood in a quite simple way by considering the modification of the  $d$  band when going from the bulk to the surface plane in two steps. The first step is the narrowing, according to (3.7), while  $\varepsilon_d$  is held constant; this narrowing leads to an increase of  $Z_d$ ,  $\delta Z_1$ , proportional to  $\varepsilon_F - \varepsilon_d$ . Then the second step is a shift  $\Delta\varepsilon_d$  of  $\varepsilon_d^{(0)}$  towards  $\varepsilon_F$  in order to decrease  $Z_d^{(0)}$  by an amount  $\delta Z_2$ . Equation (3.15) corresponds to a complete cancellation:  $\delta Z_d^{(0)} = \delta Z_1 + \delta Z_2 = 0$ ; then the shift  $\Delta\varepsilon_d$  is

TABLE II.  $\delta Z_d^{(0)}$  and  $\Delta\varphi_d^{(0)}$  (in eV). (a) The contribution  $\varphi_s(z^{(0)})$  to  $\Delta\varepsilon_d^{(0)}$  is neglected. (b) The contribution  $\varphi_s(z^{(0)})$  is calculated by using the density profile (3.16) for the conduction electrons.

	$10^2\delta Z_d^{(0)}$ (a)	$\Delta\varphi_d^{(0)}$ (a)	$10^2\delta Z_d^{(0)}$ (b)	$\Delta\varphi_d^{(0)}$ (b)
Ag(111)	0.65	0.552	0.65	0.552
Ag(100)	1.02	0.746		0.738
Ag(110)	1.85	0.931	1.26	0.624
Cu(111)	0.39	0.318	0.39	0.318
Cu(100)	0.67	0.431		0.331
Cu(110)	1.34	0.538	0.58	-0.227

closely related to  $Z_1$  and is, therefore, proportional to  $\varepsilon_F - \varepsilon_d$ . Such a scheme assumes that  $\delta Z_d^{(0)} \ll 1$  and this is precisely what we find by solving Eqs. (3.10), (3.11), (3.13), and (3.14) self-consistently, in agreement with Allan's calculations.<sup>29,30</sup>

The other remark concerning (3.15) is the dependence of  $\Delta\varphi_d^{(0)}$  on the crystallographic orientation of the surface plane. From (3.15) one gets  $\Delta\varphi_d^{(0)}(111) > \Delta\varphi_d^{(0)}(100) > \Delta\varphi_d^{(0)}(110)$ , which is opposite the dependence of the experimental work function for all the fcc metals.

We now take into account the extra potential drop  $\varphi_s(z^{(0)})$  in  $\Delta\varepsilon_d^{(0)}$  due to the conduction electrons [see Eq. (3.11)]. We have solved Eqs. (3.10), (3.11), (3.13), and (3.14) self-consistently, including the contribution  $\varphi_s(z^{(0)})$  calculated with a monotonic density profile for the conduction electrons given by Eq. (3.16) of the following section. The main result is that the dependence of  $\Delta\varphi_d^{(0)}$  with the crystallographic orientation is reduced when compared to (3.15) (see Table II). Indeed, since we do not consider the Friedel oscillations in the density profile (which is justified in the range of density that we deal with,  $r_s \sim 2.5$ ), we have  $\varphi_s(z^{(0)}) > 0$ , and  $\varphi_s(z^{(0)})$  is the larger the less close packed the surface plane. Hence we get for  $\Delta\varphi_d^{(0)} = [\Delta\varepsilon_d^{(0)} - \varphi_s(z^{(0)})]$ , a dependence less important and even inverted on the crystallographic orientation of the surface plane. The results are given in Table II. We find that  $\Delta\varphi_d^{(0)}$  is nearly independent of the orientation for Ag and takes a similar value for Cu(111) and Cu(100). The result for Cu(110) is not satisfactory. Indeed, the (110) face can be considered to be an open face and, in that case, the treatment for the conduction electrons that we use for calculating  $\varphi_s(z^{(0)})$  is certainly oversimplified. Nevertheless, we think that taking into account  $\varphi_s(z^{(0)})$  makes  $\Delta\varphi_d^{(0)}$  only weakly dependent on the surface orientation and, moreover,  $\varphi_s(z^{(0)})$  gives only a negligible contribution in the case of the (111) face. Accordingly, for  $\Delta\varphi_d^{(0)}$  we use the same value for the three low-index faces, as calculated on the (111) face. Thus we take  $\Delta\varphi_d^{(0)} = 0.55$  eV for Ag and 0.33 eV for Cu. In the case of Cu(100) a similar result was obtained by Fujiwara,<sup>33</sup>  $\Delta\varphi_d^{(0)} = 0.41$  eV, from a LMTO-ASA (ASA denotes atomic-sphere approximation) calculation.

### B. Simple-metal contribution

We are now concerned with the calculation of the work function of the effective simple metal which is

characterized by the valence  $Z_s$ . The electron-ion interaction is represented by the well-known Ashcroft pseudopotential,<sup>34</sup> which leads to satisfactory results in the case of simple metals. For the radius  $r_c$  of the pseudopotential we use the values calculated by Wills and Harrison from the minimization of the total energy at the equilibrium volume<sup>31</sup> ( $r_c = 0.869$  a.u. for Cu and 0.85 a.u. for Ag). In the literature the surface properties of simple metals have been extensively studied and we just present briefly our treatment here.

To avoid the difficult task of solving the Schrödinger equation, following the method introduced by Smith,<sup>35</sup> we use trial density profile for the conduction electrons depending on variational parameters which are determined by the minimization of the surface energy functional. We choose the density profile introduced by Badiali *et al.*<sup>36</sup>

$$n(z) = \begin{cases} n_0(1 - Ae^{\alpha z}), & z < z_0 \\ n_0Be^{-\beta z}, & z < z_0 \end{cases} \quad (3.16)$$

where  $n_0$  is the bulk electronic density. Because of the electroneutrality of the system and the continuity of both the density and its first derivative at  $z = z_0$ , we have the relations

$$\begin{aligned} A &= \frac{e^{-\alpha z_0}}{1 + \alpha/\beta}, \\ B &= \frac{e^{\beta z_0}}{1 + \beta/\alpha}, \\ z_0 &= \frac{1}{\alpha} - \frac{1}{\beta}. \end{aligned} \quad (3.17)$$

Hence two parameters, say  $\alpha$  and  $\beta$ , are independent. When the metal carries a charge  $q$  per unit of surface, the dependence of  $A$  and  $B$  on  $\alpha$ ,  $\beta$ , and  $z_0$  remains unchanged while  $z_0$  is modified and becomes

$$z_0 = \frac{1}{\alpha} - \frac{1}{\beta} - \frac{q}{n_0}. \quad (3.18)$$

The surface energy functional is of the form

$$\sigma[n] = \sigma_k[n] + \sigma_{xc}[n] + \sigma_{es}[n] + \sigma_{ps}[n] + \sigma_{cl}, \quad (3.19)$$

where the first two terms are, respectively, the kinetic energy and the exchange-correlation contributions. For the kinetic energy term, we use a gradient expansion up to

second order,

$$\sigma_k[n] = \sigma_k^{(0)}[n] + \sigma_k^{(1)}[n] + \sigma_k^{(2)}[n]. \quad (3.20)$$

$\sigma_k^{(0)}$  is the Thomas-Fermi contribution;  $\sigma_k^{(1)}$  and  $\sigma_k^{(2)}$  are the first- and second-order terms given by Smith<sup>35</sup> and by Ma and Sahni.<sup>37</sup> For the exchange-correlation energy we use the local-density approximation<sup>8</sup> with the Slater approximation for the exchange term and the Pines-Nozières expansion for the correlation term.  $\sigma_{es}$  is the electrostatic surface energy of the electrons immersed in a semi-infinite background of positive charge (jellium) and  $\sigma_{ps}$  is the term due to the pseudopotential,

$$\sigma_{ps} = \int n(z) \delta V_{ps}(z) dz, \quad (3.21)$$

where  $\delta V_{ps}$  is the difference between the sum of the electron-ion pseudopotentials averaged along the surface and the electrostatic potential of the jellium.  $\sigma_{cl}$  is the cleavage term which does not depend on the variation of the electronic density and thus does not enter in the minimization.

In order to compute the work function  $\Phi_{MS}$ , we use the so-called "change-in-self-consistent-field" expression first derived by Lang and Kohn<sup>2</sup> and later by Monnier *et al.*,<sup>10</sup>

$$\Phi_{\Delta SCF} = \left. \frac{\partial \sigma(q)}{\partial q} \right|_{q=0}, \quad (3.22)$$

where  $\sigma(q)$  is the surface energy of the charged metal. This expression has the advantage of being of second order in the error ( $\delta n$ ) of the density profile  $n(z)$ , as opposed to the expression derived from Koopman's theorem. This is of great importance in the present calculation since our density profile is not calculated from the Schrödinger equation and, in particular, it cannot produce the Friedel oscillations.<sup>3,5</sup> The work function calculated from (3.22) by using the electronic density profile (3.16) has been shown to be very close to the complete calculation of Lang and Kohn<sup>2</sup> for the jellium model<sup>11</sup> and to more refined treatments<sup>38</sup> for the simple metals.<sup>39</sup>

#### IV. RESULTS AND DISCUSSION

Our results for the work function are given and compared to experiments in Table III. We have to mention that, if the work function of Ag seems to be well established,<sup>40-42</sup> this is not the case of Cu, for which there is a rather wide dispersion between the different results in the literature.<sup>43-45</sup> This is certainly due to the difficulties encountered with Cu in order to get well-defined and cleaned surfaces.<sup>46</sup> Concerning our results, although the contribution of the  $d$  band is roughly estimated, the agreement with experiment is satisfactory in light of the simplicity of the model; indeed, the difference with experiment is about 15% for Cu and 5% for Ag. This agreement is comparable to that one obtains for the simple metals by using the simple jelliumlike models. Hence it is certainly necessary to consider a more sophisticated treatment for the conduction electrons, and not only a more refined treatment for the  $d$  band, in order to improve the present results. On the other hand, we do not reproduce quantitatively the variation of  $\Phi$  with the crystallographic orientation of the surface plane. Nevertheless, due to the effective simple-metal part, the sequence  $\Phi(111) > \Phi(100) > \Phi(110)$  is reproduced. On the other hand, in order to estimate the importance of the  $d$  band on the value of  $\Phi$ , we have calculated  $\Phi$  with a pure simple-metal treatment (denoted  $\Phi_0$ ) by using  $Z_s = 1$  and the values of  $r_c$  given by Lang and Kohn.<sup>2</sup> The comparison of  $\Phi_0$  with  $\Phi$  and  $\Phi_{\text{expt}}$  is also given in Table III and shows that the  $d$  band leads to an increase of about 20% of the work function and that our treatment is a real improvement compared to the pure simple-metal treatment.

In the framework of the present model we could calculate the surface energy  $\sigma$  which includes the surface energy  $\sigma_{MS}$  of the effective simple metal (see Sec. III) and a  $d$ -band contribution  $\sigma_d$  calculated from the  $d$ -band LDOS. However, in contrast to the case of the work function the  $d$ -band contribution to the surface energy depends explicitly on the shape of the LDOS. Moreover, since  $\sigma_d$  is the difference between the energy of the occupied states of the surface  $d$  band and of the bulk  $d$  band (corrected of the electrostatic double counting<sup>28,29,32</sup>), a

TABLE III. Work function in eV.  $\Phi_{MS}$  is the effective simple-metal contribution;  $\Phi_0$  is the pure simple-metal work function. Experimental work function taken from (a) Ref. 43; (b) Ref. 44; (c) Ref. 45; (d) Ref. 40; (e) Ref. 42.

	$\Phi_{MS}$	$\Phi$	$\Phi_0$	(a)	$\Phi_{\text{expt}}$ (b)	(c)
Cu(111)	3.92	4.24	3.78	4.63	4.94	4.98
Cu(100)	3.80	4.12	3.66	4.45	4.59	4.83
Cu(110)	3.66	3.98	3.51	4.40	4.48	4.45
				(d)	(e)	
Ag(111)	3.85	4.40	3.57	4.46	4.49	
Ag(100)	3.74	4.29	3.46	4.22		
Ag(110)	3.55	4.10	3.30	4.14		

very large cancellation is expected. Therefore,  $\sigma_d$  is very sensitive to the model used for the  $d$ -band LDOS; accordingly, we think that our model is unsuitable for the calculation of the surface energy of Cu and Ag.

Finally, we emphasize that the present model improves the electronic description of the metal provided by both the simple-metal model of Lang and Kohn<sup>1-3</sup> and the model introduced by Wills and Harrison<sup>31</sup> which includes the  $d$  band. Indeed, two important energy positions are now properly reproduced: the Fermi level relative to the bottom of the conduction band and the position of the  $d$ -band center. Moreover, when going from the bulk to the surface plane we reproduce both the narrowing of the  $d$

band and the shift in the  $d$ -band center, which are obtained in *ab initio*-like calculations.

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\*Temporary address: Dynamique des Interactions Moléculaires, Université Pierre et Marie Curie, 4 place Jussieu, 75230 Paris CEDEX 05, France.

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