Self-consistent weighted-density approximation for the electron gas. II. The metal surface

E. Chacón and P. Tarazona
Instituto de Ciencia de Materiales, Consejo Superior de Investigaciones Científicas, and Departamento de Física de la Materia Condensada, Universidad Autonoma de Madrid, Madrid E-28049, Spain
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The main properties of a metal surface in the jellium model are analyzed in the weighted-density approximation (WDA). It is found that the choice of the electron-electron pair function used in the theory is crucial to the evaluated properties. The image-potential form of the exchange and correlation potential may be recovered only with a very artificial correlation hole, which leads to unphysical results for both the location of the image plane and the surface energy. The self-consistent version of the WDA developed in the previous paper which does not need any external input is also used to evaluate the surface energy, with results close to the local-density approximation.

I. INTRODUCTION

The density-functional formalism (DFF) of Hohenberg, Kohn, and Sham,[1,2] provides a useful tool for the study of systems with inhomogeneous electron density like a metal surface. The simplest theory within this approach, the local-density approximation (LDA), has been used to evaluate most of the properties of these systems with remarkable success.[3] However, in the last few years the interest in the study of metal surfaces has been shifted towards problems like tunneling[4,5] behavior and the presence of surface image states[6] which are beyond the capability of the LDA. This has increased the search for improvements in the density-functional models used to describe the exchange and correlation (XC) energy, $E_{\rm XC}[n]$, and in particular for a correct description of the image potential far outside the metal. The weighted-density approximation (WDA) originally developed by Gunnarsson, Jonson, and Lundqvist[7] has become a very popular candidate for this task, especially since Gunnarsson and Jones[8] provided an empirical form for the XC hole to be used in the WDA in order to recover the image potential. This version of the WDA has been used to evaluate the properties of many systems,[9–12] including the position of the image plane in the jellium model for a metal surface.[13] However, there has been no careful study of the possible implications that the choice of the XC hole may have in the studied properties. Results for the surface energy with this empirical correlation hole had not been reported until now; they cast very serious doubts on the model. Moreover, we have shown that the position of the image plane given by the WDA, with the empirical XC hole of Gunnarsson and Jones,[8] is unphysical and artificially fixed. In our previous paper[14] (hereafter referred to as paper I), we proposed a self-consistent way to obtain the XC energy and the pair distribution function within the WDA. The theory, which we called the self-consistent weighted-density approximation (SC-WDA), does not require any external input, so it should be regarded as a good candidate to check the accuracy of the whole scheme. This paper is divided into two parts; in the first one we analyze the capability of the WDA in reproducing the image potential, and in the second part we compare the results for the surface energy given by the different versions of the WDA and the SC-WDA. The results are also compared with the LDA and other recent calculations[15,16] with a different approach outside the DFF.

II. THE IMAGE POTENTIAL IN THE WDA

A charged particle close to a metal is attracted towards the metal surface by the classical image potential,[17]

$$V(z)=-\frac{1}{4(z-z_0)}\ , \tag{2.1}$$

where the z axis is normal to the surface with the bulk metal at $z<0$ and z_0 is the position of the image plane. Atomic units $m_e=e=\hbar=1$ are used throughout the paper. In principle, the image potential should be recovered from the DFF as the limit for very large z of the exchange and correlation (XC) potential, defined as

$$V_{\rm XC}(\mathbf{r})=\frac{\delta E_{\rm XC}[n(\mathbf{r})]}{\delta n(\mathbf{r})}\ . \tag{2.2}$$

The idea is that $V_{\rm XC}(\mathbf{r})$ describes the potential acting on an electron at $\mathbf{r}$ due to the correlation hole created by all the other electrons. For an electron located far from the metal the effect should be equivalent to that of a test charge described in (2.1), so that the large-z limit of (2.2) should approach (2.1). This is a very tough test for any density-functional model used to describe $E_{\rm XC}[n]$, because it requires an accurate treatment of the electron-electron correlations in a strongly inhomogeneous system. Simple models like the local-density approximation (LDA) fail to reproduce this behavior, giving exponential

decay for $V_{XC}(z)$ instead of the $1/z$ form of (2.1). The weighted-density approximation (WDA) developed by Gunnarsson *et al.*[7] seems to be a better candidate to reproduce this effect. It starts with the XC energy written as

$$E_{XC}[n]=\tfrac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}G(|\mathbf{r}-\mathbf{r}'|,\bar{n}(\mathbf{r}))\ , \tag{2.3}$$

where $G(r,n)$ is the XC hole in a homogeneous system of density n, integrated along a path (from $\gamma=0$ to 1) which depends on the Coulomb interactions (see I for details)

$$G(r,n)=\int_0^1 d\gamma[g(r,n,\gamma)-1]\ . \tag{2.4}$$

The averaged density, $\bar{n}(r)$, at which $G(r,n)$ is evaluated in (2.3), is fixed by the normalization of the hole

$$\int d\mathbf{r}'\,n(\mathbf{r}')G(|\mathbf{r}-\mathbf{r}'|,\bar{n}(\mathbf{r}))=-1\ . \tag{2.5}$$

The XC potential given by the functional derivative of (2.3) is

$$\begin{aligned}V_{XC}(\mathbf{r})=&\tfrac{1}{2}\int d\mathbf{r}'\frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}G(|\mathbf{r}-\mathbf{r}'|,\bar{n}(\mathbf{r}))\\&+\tfrac{1}{2}\int d\mathbf{r}'\frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}G(|\mathbf{r}-\mathbf{r}'|,\bar{n}(\mathbf{r}'))\\&+\int d\mathbf{r}'\,n(\mathbf{r}')G(|\mathbf{r}-\mathbf{r}'|,\bar{n}(\mathbf{r}'))F(\mathbf{r}')\ ,\end{aligned} \tag{2.6}$$

where

$$F(\mathbf{r})=\frac{\displaystyle\int d\mathbf{r}'\frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\frac{dG(|\mathbf{r}-\mathbf{r}'|,\bar{n}(\mathbf{r}))}{d\bar{n}(\mathbf{r})}}{\displaystyle 2\int d\mathbf{r}'n(\mathbf{r}')\frac{dG(|\mathbf{r}-\mathbf{r}'|,\bar{n}(\mathbf{r}))}{d\bar{n}(\mathbf{r})}}\ . \tag{2.7}$$

For a homogeneous system of density n_0, $F(r)$ becomes

$$F(r)=F(n_0)=-\epsilon_{XC}(n_0)+n_0\epsilon'_{XC}(n_0)\ . \tag{2.8}$$

The factor $n(\mathbf{r}')G(|\mathbf{r}-\mathbf{r}'|,\bar{n}(\mathbf{r}'))$ in the last two terms of (1.6) is very small unless $\mathbf{r}'$ is inside the metal, so that for points far outside the metal surface we have (see Appendix D of Ref. 7)

$$\begin{aligned}\lim_{z\to\infty}V_{XC}(z)=&\pi\int_{-\infty}^0 dz_1 n(z_1)\int_{z-z_1}^\infty dR\ G(R,\bar{n}(z))\\&+\pi n_0\int_{-\infty}^0 dz_1\int_{z-z_1}^\infty dR\ G(R,n_0)\\&-2\pi n_0F(n_0)\\&\times\int_{-\infty}^0 dz_1\int_{z-z_1}^\infty dR\ RG(R,n_0)\ .\end{aligned} \tag{2.9}$$

If the XC hole, $G(r,n)$, decays faster than any inverse power for large r, it is easy to see that the last two terms in (2.9) are also short ranged. The normalization requirement (2.5) for very large z may only be fulfilled if the function $G(r,\bar{n}(r))$ extends up to distances of order z, and this requires very small values of $\bar{n}(z)$, because the main dependence of $G(r,n)$ is through the scaled variable $rn^{1/3}$. In the first term of (2.6) the largest contribution to the integral comes from points $r'\ll r$ and we may approximate $1/[\mathbf{r}-\mathbf{r}'|$ by $1/z$. The result is, using (2.5), that for $z\to\infty$ the XC potential in the WDA approaches[7]

$$\begin{aligned}V_{XC}(z)=&\tfrac{1}{2}\int d\mathbf{r}'\,n(\mathbf{r}')\frac{G(|\mathbf{r}-\mathbf{r}'|,\bar{n}(\mathbf{r}))}{|\mathbf{r}-\mathbf{r}'|}\\=&-\frac{1}{2z}+(\text{faster decaying terms})\ .\end{aligned} \tag{2.10}$$

Thus the WDA with a short-ranged XC hole gives the correct power law for the image potential but with a coefficient wrong by a factor of 2. This was the result obtained in the original work by Gunnarsson *et al.*[7] and it will also be the case if the SC-WDA result of our previous work (paper I) is used. However, the coefficient in (2.10) changes if the function $G(r,n)$ has a power-law decay for large r. In this case the center of gravity of $n(\mathbf{r}')G(|\mathbf{r}-\mathbf{r}'|,\bar{n}(\mathbf{r}))$ does not remain in the surface region and the expression

$$V_{XC}(z)=-\frac{\nu-3}{2(\nu-1)z}+\cdots \tag{2.11}$$

may be easily obtained for large z, where ν is the decay power of $G(r,n)$. The correct coefficient of the image plane is obtained for $\nu=5$, and on this basis Gunnarsson and Jones[8] proposed a very simple ansatz

$$G(r,n)=C(n)\hat{G}[r2k_F(n)/\lambda(n)]\ , \tag{2.12}$$

with the usual definition of the Fermi wave vector k_F and

$$\hat{G}(y)=1-\exp(-1/y^5)\ , \tag{2.13}$$

where $C(n)$ and $\lambda(n)$ are determined to satisfy the normalization requirement (2.5) and a given XC energy per electron in a homogeneous system through (2.3). The two conditions may, in general, be expressed as

$$\lambda(n)=(9\pi/4)^{1/3}\frac{A_2}{A_1r_s\epsilon_{XC}(r_s)} \tag{2.14}$$

and

$$C(n)=A_2\frac{8k_F(n)^3}{n\lambda(n)^3}\ , \tag{2.15}$$

where the constants A_1 and A_2 are defined as

$$1/A_1=\int d\mathbf{y}\frac{\hat{G}(|\mathbf{y}|)}{|\mathbf{y}|} \tag{2.16}$$

and

$$1/A_2=-\int d\mathbf{y}\,\hat{G}(|\mathbf{y}|)\ . \tag{2.17}$$

The WDA with the XC hole defined in (2.12) and (2.13) has been used previously to evaluate the properties of metal surfaces, including the position of the image plane.[13] However, it may be shown that the correct coefficient of the image potential is obtained by this model only in a very artificial way, leading to unphysical results for the position of the image plane. If we assume that the XC energy used in (2.14) has the correct low-

density limit, $\epsilon_{XC}(n) \propto 1/r_s$ as $r_s \to \infty$, then both $C(n)$ and $\lambda(n)$ go to a constant value for small n and the normalization condition (2.5) becomes

$$-1=\frac{A_2}{\bar{n}(z)}\int_0^\infty dz_1 n[z-z_1/K(\bar{n}(z))]2\pi\int_{z_1}^\infty dy\, y\hat{G}(y)\ , \tag{2.18}$$

where $K(n)=2k_F(n)/\lambda(n)$. The decay law for $n(z)$ at large z may be easily obtained from this equation by making use of the following result. Given any function of z, like the electronic density in a metal surface $n(z)$, which goes to a bulk value n_0 as $z\to\infty$ and to zero as $z\to 0$, we have that

$$\int d\mathbf{r}'\frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^m}=\frac{2\pi n_0}{(m-2)(m-3)}\frac{1}{z^{m-3}}+\frac{2\pi p_1}{z^{m-1}}+O\left[\frac{1}{z^m}\right] \tag{2.19}$$

for $m>3$, and with the only condition the existence of the first moment,

$$p_1=\int_{-\infty}^\infty dz\, z[n(z)-n_0\Theta(z)]\ . \tag{2.20}$$

$\Theta(z)$ is the Heaviside step function, and the origin of the z axis is fixed to get a vanishing zero-order moment, which in the case of the jellium model of a metal surface corresponds to the edge of the positive charge background. With this result and assuming that the scaled function $\hat{G}(y)$ in (2.12) varies as

$$\hat{G}(y)=\frac{A}{y^5}+\frac{B}{y^{10}}+\cdots \tag{2.21}$$

at large y [as is the case of (2.13)], Eq. (2.18) becomes

$$-\frac{\bar{n}(z)}{2\pi A_2 n_0}=\frac{A}{[zK(\bar{n}(z))]^2}+\frac{A}{[zK(\bar{n}(z))]^2}\frac{p_1}{z^2}+\cdots\ , \tag{2.22}$$

and

$$\lim_{z\to\infty}\bar{n}(z)=C_1 z^{-6/5}(1+C_2 z^{-2}+\cdots)\ , \tag{2.23}$$

where $C_1=n_0(-2\pi A A_2/[6K(n_0)])^{3/5}$ and $C_2=18/5p_1$. This result may now be introduced in Eq. (2.9) to extend the analysis of Gunnarsson and Jones[7] up to the next-to-leading order, to obtain after some algebra

$$\lim_{z\to\infty}V_{XC}(z)=-\frac{1}{4z}\left[1+\frac{6p_1}{n_0 z^2}+\cdots\right]+\left[\frac{D}{16z^3}\frac{1}{[\epsilon_{XC}(n_0)]}+\cdots\right]+\left[-\frac{D}{4z^2}\frac{\epsilon_{XC}(n_0)-n_0\epsilon'_{XC}(n_0)}{[\epsilon_{XC}(n_0)]^2}+\cdots\right], \tag{2.24}$$

where the large parentheses correspond to the respective terms on the right-hand side of (2.6). The constant $D=-2\pi A A_2^3/(6A_1^2)$ depends only on the form chosen for the function $\hat{G}(y)$. The position of the image plane, z_0, in (2.1) is given by the coefficient of z^{-2} in (2.24), the result being

$$z_0=D\frac{\epsilon_{XC}(n_0)-n_0\epsilon'_{XC}(n_0)}{[\epsilon_{XC}(n_0)]^2}\ , \tag{2.25}$$

which does not depend on p_1 or on any other detail of the electronic density distribution at the surface, being fixed by the bulk density and the constants A, A_1, and A_2 set by the choice of the XC hole. In particular, z_0 is proportional to the coefficient A for the $1/y^5$ tail of $\hat{G}(y)$, which was introduced *ad hoc* without any physical interpretation. This may be expected because the correct coefficient in (2.11) is only obtained if the center of gravity of the correlation hole is driven towards the bulk metal by the slow decay of $\hat{G}(y)$, so that the surface structure becomes irrelevant. It has to be pointed out that the direct evaluation of the image plane from the numerical evaluation of $V_{XC}(z)$ in a WDA calculation may lead to large numerical errors, so that there are published results for z_0 which do not agree with this analytical value.[13] However, it has been checked that far enough from the surface, the results of the asymptotic formula are recovered by a careful numerical evaluation.[18] If the function $\hat{G}(y)$ were chosen to have a next-to-leading decay term like $1/r^6$ instead of the form (2.21) taken by Gunnarsson and Jones,[8] the result for $V_{XC}(z)$ at large z would be

$$V_{XC}(z)=-\frac{1}{4z}(1+\text{const}\times z^{-3/5}+\cdots)\ , \tag{2.26}$$

so that there is not even a well-defined image plane. Altogether, it is clear that although the WDA is qualitatively better than the LDA in the description of the potential outside a metal surface, it is still not able to give a full account of the image potential. The reason for this comes from the use of a spherical XC hole in (2.3) (corresponding to a system of homogeneous density n), while the actual XC hole for an electron outside the metal should flatten in the interfacial region.[19] There is an alternative way to obtain the image plane within the DFF, through the evaluation of the centroid of the charge induced by an external field. This route is much easier to follow and even the simple LDA then gives well-behaved values of z_0, which of course depend on the surface structure and hence have to be evaluated self-consistently. A good density-functional model for $E_{XC}[n]$ should give the same result through the two routes. It is clear, however, that the WDA is still far from this task. The *ad hoc* $1/y^5$ decay required to obtain the exact coefficient in the leading term of $V_{XC}(z)$ should be regarded as an artificial way to correct an intrinsic defect at the price of getting clearly unphysical results like the image plane given by (2.25). The $1/y^5$ decay is also inconsistent with the small q behavior of the structure factor, $S(q)$, directly related to the Fourier transform of $G(r,n)$. This limit should be directly given by the plasmon frequency[14] and this is only possible if

TABLE I. Exchange and correlation surface energy, σ_{XC} (in ergs/cm^2), in the infinite-barrier model. The results of our SC-WDA are compared with the "exact" RPA of IW-LP (Refs. 20 and 21), the original results of the WDA with the RPA hole (Ref. 7), and those obtained with the empirical form (2.13) E-WDA (Wigner's interpolation formula for the correlation energy was used in this case). The different local-density values correspond to the use of the respective functions $\epsilon_{XC}(n)$.

r_s	SC-WDA	LDA	WDA RPA	Exact RPA	LDA RPA	E-WDA Wigner	LDA Wigner
2.07	1459.9	1235.2	585.0	1388.0	1241.0	−108.9	1171.7
4.0	205.7	180.7	102.0	203.0	184.0	−14.8	175.2
6.0	62.1	55.4		63.0	58.0	−1.1	55.6

$\hat{G}(y)$ decays faster than $1/y^7$. We believe that the behavior (2.10) has to be accepted as an intrinsic limitation of the WDA and the correlation hole used within this functional model should be taken to decay exponentially rather than by any artificial inverse power law.

III. THE METAL SURFACE ENERGY IN THE WDA

Several versions of the WDA have been applied to the study of atoms,[9] bulk metals and semiconductors,[10–12] with fairly good results. However, this approximation has been scarcely used to get the surface energy of metals. In the original paper where the WDA was developed, Gunnarsson *et al.*[7] obtained the surface energy, within the jellium model of a metal, using the random-phase approximation (RPA) pair correlation function. The WDA has later been applied to study the XC potential in metal surfaces, as described in the preceding section, using the correlation hole proposed by Gunnarsson and Jones,[8] but no result for the surface energy had been reported in this case. The XC surface energy

$$\sigma_{XC}=\int_{-\infty}^{\infty} dz\, n(z)[\epsilon_{XC}(z)-\epsilon_{XC}(-\infty)] \tag{3.1}$$

is indeed a difficult quantity to evaluate; first of all because it is associated with a region of strongly varying electron density, and also the integration over a semi-infinite system gives a large effect to any slight misrepresentation. This is the reason that while the atomic energies evaluated with different descriptions of $G(r,n)$, within the WDA, always give very close results, the surface energies may depend strongly on the XC hole used. That makes the evaluation of σ_{XC} very interesting as a test of the different versions of the WDA. In this section we compare the results of the original WDA with different descriptions of the correlation hole, and the results given by the SC-WDA we have developed in paper I. All the calculations refer to the jellium model, where the positive charge of the ions is replaced by a steplike background with uniform density in the metal and zero outside. First of all, because of its numerical simplicity and in order to compare with the original results of Gunnarsson *et al.*,[7] we have calculated the surface energy in the infinite barrier model. In Table I we present those results for the XC contribution to the surface energy using the original WDA (Ref. 7) with the RPA bulk correlation function, the results of the SC-WDA, and those of Inglesfield and Wikborg[20] modified by Langreth and Perdew[21] (IW-LP), which are often quoted as exact although they include the correlation energy within the RPA.[22] The results of the LDA are also included, as well as those of the WDA using the empirical XC hole (2.13). Our SC-WDA gives values of σ_{XC} very close to those of IW-LP, both being about 10% above the LDA. The original calculation with the WDA using the RPA correlation hole,[7] gives results too low (by a factor of 2), while the WDA with the empirical XC hole gives completely unreliable negative σ_{XC}. This is due to the $1/y^5$ decay, artificially introduced to obtain the image potential, which extends the surface effects too far into the bulk.

In order to study the influence that self-consistency in the calculation of the density profiles may have in the evaluation of the total surface energy, σ, we have also performed the calculation for the density profiles given by the finite-barrier model,[23] for several values of the barrier height, V_0. An approximative variational estimation of the minimum surface energy with respect to V_0 gives values of σ for the LDA and the SC-WDA much closer than in the case of the infinite-barrier model (Table II). This may be understood because as $n(z)$ becomes smoother, the surface energy is more dominated by the small q behavior of the response function. In Fig. 1 we present the XC contribution to the response function, $U_{XC}(q,n)$ [see Eqs. (1.12) and (1.13) in paper I], from the SC-WDA which is quite flat for q up to $2k_F$. This means that σ_{XC} should be close to the value given by the LDA, which approximates $U_{XC}(q,n)$ by its constant value at $q=0$. The very poor results of the WDA with the empirical XC hole (2.13) may also be understood from the function $U_{XC}(q,n)$ given by this ap-

TABLE II. Surface energy σ (in ergs/cm^2) obtained in the variational calculation for the finite-barrier model. The results of our SC-WDA are compared with the local density (LDA) using the same function $\epsilon_{XC}(n)$. V_0 is the value of the barrier height which minimizes σ in each case. V_0 is in units of the Fermi energy.

	SC-WDA		LDA	
r_s	V_0	σ	V_0	σ
2	1.00	−267.4	1.00	−276.5
3	1.00	261.9	1.00	257.9
4	1.15	175.4	1.23	171.6
5	1.33	106.0	1.48	102.7
6	1.64	66.5	1.84	64.3

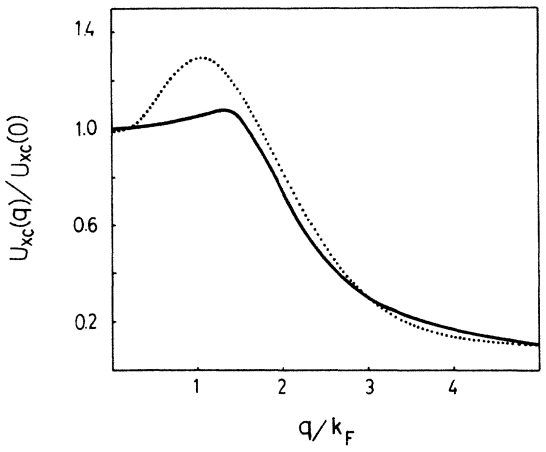

FIG. 1. Comparison between the functions $U_{XC}(q,n)$ for $r_s=5$ obtained in the SC-WDA (Ref. 14) (solid line) and that using the WDA with the empirical correlation hole (2.13) (dotted line). The functions are normalized to the $q=0$ value.

proach (see Fig. 1). We have also performed calculations with the WDA using different forms of the XC hole to fit [through Eq. (2.15) of paper I] other possible functions $U_{XC}(q,n)$, like those of Vashista and Singwi[24] and Utsumi and Ichimaru.[25] σ_{XC} depends strongly on the response function used, confirming the idea that the small q behavior of $U_{XC}(q,n)$ is of crucial importance for the evaluation of the surface energy. There are not, at the present, exact results for the function $U_{XC}(q,n)$, so that it would be difficult to decide which one to use in the WDA. We believe that, because of its internal consistency, the SC-WDA provides the best possible choice, giving probably the most accurate results for σ_{XC} within this scheme.

Recent calculations of the surface energy of the jellium model by Sun *et al.*[26] and Krotscheck *et al.*[15,16] in the correlated basis function approach have important differences from the LDA. This approach is quite different from any application of the DFF. Instead of attempting a full representation in terms of the density distribution, it uses a variational approach directly for the electron-electron correlation. The results confirm that most of the possible evaluations of the surface energy give values very close to the LDA,[15] but if the kinetic energy contribution to the correlation is properly taken into account at the surface, σ_{XC} becomes much larger. The SC-WDA takes into account the kinetic energy contribution to $E_{XC}[n]$ through the integration of the coupling parameter γ in (2.4).[27] For a bulk metal this is probably done quite accurately, given the excellent results obtained for $\epsilon_{XC}(n)$ in the self-consistent calculation. However, the use of the spherically symmetric $g(r)$ in the surface may neglect possible surface effects in this contribution. As in the study of the image potential, this fact points towards the need of using nonspherical XC holes at the surface in order to achieve a full accurate description of the surface effects within the DFF.

IV. CONCLUSIONS

We have analyzed the capability of the WDA for the study of the surface properties of metals. Our first conclusion is that this density-functional model may only be used after a careful choice of the electron-electron correlation hole, which is the main input necessary in the original version of the theory. We have shown that the empirical form (2.13), introduced to recover the correct image potential outside the metal, achieves this only in a very artificial way, leading to unphysical results for the position of the image plane. Moreover, the surface energies given by that version of the WDA, which had not been reported until now, are completely unreasonable. Thus the existing results for surface properties within the WDA using this empirical XC hole[13] should be regarded with caution. With respect to the image potential limit of $V_{XC}(z)$ outside the metal, it is clear that the WDA gives an important improvement over simpler models like the LDA, being able to reproduce the $1/z$ decay. Thus it could be used to study some qualitative aspects which are beyond the LDA. However, it is still not possible to recover the correct numerical coefficient of the decaying tail in a natural way, i.e., with a well-behaved XC hole. This has to be considered as an intrinsic limitation of the WDA, associated with the use of a spherically symmetric correlation hole, which is not worth improving at the price of an artificial choice of $g(r)$. The evaluation of the surface energy within the WDA depends strongly on the correlation hole used. The SC-WDA, that we have developed in paper I, gives probably the best possible results within the WDA scheme, and it gives σ_{XC} very close to the LDA. It is still not clear whether or not the crude LDA is so close to the exact values for σ_{XC} that more sophisticated theories have to give essentially the same results. However, it is sure that some versions of the WDA give values of σ_{XC} very far from LDA, while more careful treatments within the same scheme get very close to it. Deviations from the LDA results have been reported from correlated basis function calculations,[15] and they seem to be associated with the surface excess of the kinetic energy contribution to the correlation energy. It may be possible that this effect is missing in the WDA again because of the use of spherical pair correlation functions. This is the main feature to be corrected in any improved density-functional model for $E_{XC}[n]$ along the lines of the WDA.

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