

Self-consistent image potential in a metal surface

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Electron densities and effective potentials at a jellium surface are calculated using the local-density (LD) approximation inside the metal and a physically based interpolation to the image potential outside. The image-plane position z_0 is also determined self-consistently, and we find only a slight contraction of z_0 with respect to the LD values of Lang and Kohn. We also provide an empirical criterion to determine z_0 from the local density.

Since its development some twenty years ago, density-functional theory¹ has undoubtedly become the most versatile and powerful scheme² for calculating the electronic structure of atoms, molecules, and solids. Within this framework, a crucial key to practical calculations has been the local-density (LD) approximation (LDA) to the exchange and correlation energy which, despite some well-known limitations, has proven to be very realistic in an enormous variety of problems.³ One of these limitations is the failure of LD effective potentials to reproduce the correct $-1/r$ image behavior outside atoms and $-1/z$ outside metal surfaces. As pointed out by Lang and Kohn,⁴ the image potential has very little influence on such properties as work functions and surface energies, because it affects only regions of space which are classically forbidden to the electrons (and consequently, which possess very small electron densities). However, the introduction of the image potential is crucial in two problems which have attracted recently much interest: The existence of image states⁵ at some metal surfaces and the tunnel current across the vacuum gap in scanning tunneling microscopy.⁶ In both cases the exact behavior of the effective potential near the surface is not as important as the correct asymptotic limit for $z \rightarrow \infty$.

A number of approaches have been tried for going beyond the LDA (Ref. 3). The achievements have not been very satisfactory for two kinds of reasons: on the one hand, the computational effort generally increases dramatically and, on the other hand, the resulting magnitudes of some physical quantities are worse than with the LDA, and sometimes even become divergent.⁷ One of the most successful approaches to nonlocal exchange and correlation is the modified version of Gunnarsson and Jones⁸ of the weighted-density approximation.⁷ This approximation clearly improves exchange-correlation energies over the LDA in atoms⁹ and solids.¹⁰ In the case of surfaces, it also approaches the correct $-1/4z$ potential as the distance to the surface $z \rightarrow \infty$. Very recently, this scheme has been applied by Ossicini *et al.* to calculate self-consistently the electronic density and effective potential at a jellium surface.¹¹ One of the most striking results of this calculation is that the image-plane position z_0 is about one Bohr closer to the surface than in the LD calculation of Lang and Kohn.⁴ However, it should be mentioned that the method of determination of z_0 is quite different in the two calculations. Lang and Kohn showed

rigorously that the image plane is located at the centroid of the excess charge induced by a uniform electric field perpendicular to the surface. It would be necessary to apply this criterion to the calculations of Ref. 11 to see whether the resulting image-plane positions are consistent with those calculated from the asymptotic behavior of $V_{xc}(z)$. In this respect, it should be noticed that, although the weighted-density approximation used gives the correct asymptotic behavior, $-1/4z$, this behavior arises from an image charge distribution which is not asymptotically correct: it is not confined to the surface, but goes deep into the bulk and is too narrow in the direction parallel to the surface. Therefore, there is no reason in principle for this approximation to give the correct value of z_0 in $-\frac{1}{4}(z-z_0)^{-1}$.

Here we will adopt a less rigorous, but simpler and much faster, approach to calculate self-consistently the electronic charge distribution and effective potential at a metal surface, including the image potential also self-consistently. In particular, we will try to shed some new light on the determination of the image-plane position, which is very important for calculating image state energies and tunnel barriers. It should be kept in mind that our intention is *not* to improve the LDA in the bulk and surface regions, but rather to complement it by including the image potential as realistically as possible in the vacuum region.

The basic idea underlying our approximation is that of electron-hole separation, which is illustrated schematically in Fig. 1. Within the metal, the exchange-correlation hole is essentially centered on the electron and the LDA approximation is adequate for most purposes. But as the electron crosses the image plane and moves outwards, the hole cannot follow, and rather it spreads laterally along the image plane. Our basic approximation is to assume that the hole shape remains unaltered, except for this lateral spreading. Thus, we write the exchange-correlation hole density as a convolution,

$$n_{xc}(\bar{x}', z'; z) = \int d\bar{x}'' n_{cl}(\bar{x}''; z) n_{xc}(\bar{x}' - \bar{x}'', z'; z_0), \quad (1)$$

where \bar{x}' and z' are coordinates parallel and perpendicular to the surface and z is the position of the electron [we take $\bar{x} = \bar{0}$ in (1)]. $n_{xc}(\bar{x}', z'; z_0)$ is the hole density when the electron is on the image plane position z_0 and we assume that this hole is spherically symmetric, as described in the

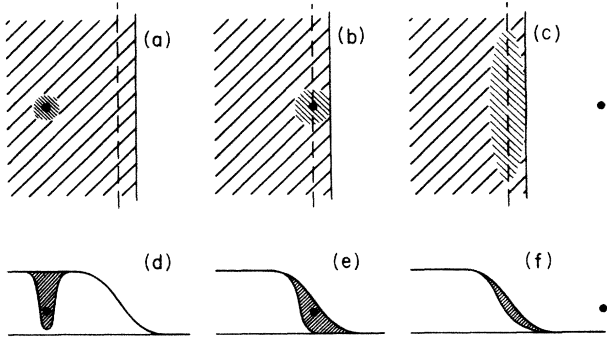


FIG. 1. (a)–(c) Schematic representation of the exchange-correlation hole shape for different electron positions (solid circle). The solid line marks the end of the electron density and the dashed line marks the image plane, where electron-hole separation begins. Before separation, the hole follows the electron, and after separation, it remains on the image plane and spreads laterally. (d)–(f) Schematic electron density profile at the surface, and hole density profiles, showing the same effect.

LDA. Thus

$$n_{xc}(\bar{x}', z'; z_0) = n_{xc}^{LD}(r; n(z_0)), \quad (2)$$

where $r = [(\bar{x}')^2 + (z' - z_0)^2]^{1/2}$. The other factor in the convolution $n_{cl}(\bar{x}''; z)$ is the classical surface charge density induced by a point charge on a conductor surface,

$$n_{cl}(\bar{x}''; z) = \frac{z - z_0}{2\pi[(\bar{x}'')^2 + (z - z_0)^2]^{3/2}}. \quad (3)$$

Notice that n_{xc} is always normalized because both terms of the convolution are already normalized. It is not difficult to show by integration that the electrostatic potential produced by the hole charge density at the position of the electron is

$$V_{xc}(z) = (z - z_0) \int_{z-z_0}^{\infty} \frac{\phi_{xc}^{LD}(r; n(z_0))}{r^2} dr, \quad (4)$$

where $\phi_{xc}^{LD}(r; n(z_0))$ is the spherical potential produced by $n_{xc}^{LD}(r; n(z_0))$. By construction, $V_{xc}(z)$ matches the local exchange-correlation potential $V_{xc}^{LD}(z)$ at $z = z_0$ and satisfies the asymptotic behavior $V_{xc}(z) \rightarrow -\frac{1}{4}(z - z_0)^{-1}$ when $z \rightarrow \infty$. In this work, we will not try to use the best possible choice for the local hole density but rather we want simply to use the present scheme to find a reasonable interpolation procedure between the LD potential in the bulk and the image potential far outside. Therefore, we will also circumvent at this stage the need of calculating the functional derivative to find the potential from a well-defined energy functional. One of the simplest analytical forms that one can use for the local hole density is

$$n_{xc}^{LD}(r; n) = \frac{b^3}{32\pi} (1 + br) e^{-br}, \quad (5)$$

which has no kink at $r=0$ and is already normalized. The decay parameter b is a function of the local density n , adjusted to give the correct value for $V_{xc}^{LD}(n)$. After integration of Poisson's equation and Eq. (4), the resulting

nonlocal (NL) potential has the form

$$V_{xc}^{NL}(x) = -\frac{1 - [1 + b(z - z_0)/4]e^{-b(z - z_0)}}{4(z - z_0)}. \quad (6)$$

Our exchange-correlation potential is then defined as $V_{xc}(z) = V_{xc}^{LD}(z)$ for $z \leq z_0$ and Eq. (6) for $z \geq z_0$. The Wigner expression is employed for local correlation. The parameter b is chosen to match continuously $V_{xc}^{LD}(z)$ at the image-plane position z_0 . This gives the condition $b = -\frac{16}{3}V_{xc}^{LD}(z_0)$. The value of z_0 is calculated self-consistently as follows.

At every iteration to self-consistency we solve Kohn-Sham¹ equations for a neutral jellium slab of sufficient thickness (100–160 Bohr) and for a slab with a small charge excess. The centroid of the excess charge in a semi-slab is then used as z_0 to calculate the potential for the next iteration. In this way we not only obtain the self-consistent density profile but also a self-consistent effective potential whose asymptotic $-\frac{1}{4}(z - z_0)^{-1}$ behavior is consistent with its own linear response.

As expected, most surface properties are nearly unaffected by the use of the nonlocal potential. Thus, the work functions change only by ~ 0.05 eV with respect to the LDA. But we are now interested in the asymptotic behavior of the effective potential for calculating image state energies and tunneling currents. Figure 2 shows the resulting self-consistent effective potential for $r_s = 5$, together with the local-density potential and with the image potential. Notice that no kink is observed for V_{xc} at $z = z_0$. Notice also that the slope $V'_{xc} = dV_{xc}/dz$ is not adjusted at z_0 by using the one-parameter form (6). It is therefore very significant that the resulting mismatch of V'_{xc} is less than 1%. In fact, the condition for perfect matching with the potential (6) is that $V_{xc}^{LD'}/V_{xc}^{LD2} = \frac{16}{9} = 1.78$ at z_0 . We have checked that the potentials calculated self-consistently by us, as well as those calculated by Lang and Kohn verify, in atomic units

$$V_{xc}^{LD'}(z_0)/V_{xc}^{LD2}(z_0) = 1.81 \pm 0.04, \quad (7)$$

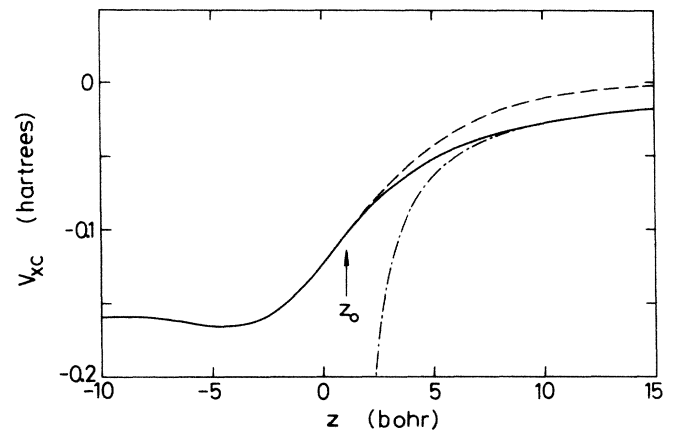


FIG. 2. Self-consistent exchange-correlation potential for $r_s = 5$, using Eq. (6) as described in the text (solid line). Dashed and dot-dashed lines show the local-density potential for the same density and the image potential, respectively. z_0 is the self-consistent image-plane position.

where z_0 is the image-plane position, taken as the centroid of the charge induced by a weak electric field. This observation, valid for all bulk densities in the range $r_s=2-5$ bohr, is very important because it provides a purely local criterion to determine (with an error of less than 0.1 Bohr) the image-plane position, which is a property of the highly nonlocal image potential.

Condition (7) can be understood in terms of electron-hole separation. We can consider V_{xc} as the interaction potential between the electron and its hole and minimize this energy as a function of the position of the hole. If we assume that V_{xc} is well represented by V_{xc}^{LD} before hole separation and by Eq. (6) after hole separation, the conditions for the point of hole separation are that $V_{xc}^{LD}(z_0-dz) \leq V_{xc}^{NL}(z_0-dz)$ and $V_{xc}^{LD}(z_0+dz) \geq V_{xc}^{NL}(z_0+dz)$. Since $V_{xc}^{LD}(z_0) = V_{xc}^{NL}(z_0)$ by construction, we obtain the condition $V_{xc}^{NL'}(z_0) = V_{xc}^{LD'}(z_0)$. Therefore, the condition of energy minimization of electron-hole interaction is that not only V_{xc} but also its first derivative must be continuous at z_0 . The division by V_{xc}^2 in Eq. (7) is then just a matter of appropriate scaling for different electron densities.

The above argument is not rigorous because we have avoided the problems of functional minimization by identifying V_{xc} as the electron-hole interaction energy, which is a simplification. We also assume that electron-hole separation begins suddenly at z_0 and this is not quite correct.¹² We believe, however, that the argument can be made more rigorous without changing the basic ideas. This will be a subject for further work but is beyond the scope of the present paper.

The results for the image-plane position are compared in Table I with those obtained with a purely local potential (which agree with those reported by Lang and Kohn⁴ and with the results of Ossicini *et al.*¹¹ with the weighted-density approximation. It can be seen that our results are very similar to the local-density ones and very different from those of Ref. 11. We think that this difference is due to the difference method of calculating z_0 rather than to the nonlocality, and we stress that the values of z_0 in Ref. 11 are not made self-consistent in the

TABLE I. Image-plane positions for different jellium densities, as calculated with the local-density approximation (LDA) and the nonlocal potentials of this work [Eq. (6)] and of Ref. 11 (which used the nonlocal scheme of Ref. 8). In the last case, the criterion for the image-plane position is different from that used in the other two calculations.

r_s	LDA	Eq. (6)	Ref. 11
2	1.57	1.49	0.85
3	1.35	1.24	0.62
4	1.25	1.13	0.45
5	1.17	1.08	0.26
6	1.10	1.02	0.06

same sense as ours are.

It is also illustrative to apply criterion (7) to the potentials of Ossicini *et al.* This gives $z_0=1.0\pm 0.3$ for $r_s=2-5$ Bohr, again similar to those of Lang and Kohn and to ours. Therefore, we believe that the nonlocal scheme used in Ref. 11 is not very appropriate for calculating the image-plane position, and, consequently, the potential at large z . Although that scheme may be better in the transition region $0 \leq z \leq 2$ Bohr, our potential gives the correct energies for the image states of several metal surfaces.¹³

Finally, two words of caution should be expressed: first, the contraction of z_0 might in principle also be due to nonlocality effects in the surface region and inside the metal; and second, criterion (7) might be closely associated with the use by us (and by Lang and Kohn) of local-density potentials of $z \leq z_0$. Therefore, a self-consistency test of the results of Ossicini *et al.* consisting of the calculation of the centroid of the charge induced by a small field would be very illuminating.

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