RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 39, NUMBER 14 15 MAY 1989-I

Evaluation of the exchange-correlation potential at a metal surface from many-body perturbation theory

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(Received 27 December 1988)

We report a first-principles evaluation of the exchange-correlation potential ($V_{\rm XC}$) at a metal surface. An integral equation relating $V_{\rm XC}$ and the nonlocal electron self-energy ($\Sigma_{\rm XC}$) is solved numerically for a free-electron metal surface, with use of a static approximation for $\Sigma_{\rm XC}$. The strongly inhomogeneous nature of the electron density profile at the surface is treated exactly, i.e., without invoking the usual local-density approximation. Our result for $V_{\rm XC}$ has the correct imagelike asymptotic behavior; it derives implicitly from a nonlocal exchange-correlation energy functional. We study the effect of nonlocality on the position of the effective image plane (z_0) from an analysis of the image tail of $V_{\rm XC}$ and also from linear-response theory. The difference in the values of z_0 obtained by both methods for low metallic densities is attributed to electron-overlap effects.

Density functional theory[1,2] has established itself as an extremely successful scheme for the study of the electronic structure of metal surfaces. The mathematical framework for this scheme is given by the Kohn-Sham (KS) equation,[1] which is a one-electron-like Schrödinger equation in which all many-body effects are introduced through the exchange and correlation (XC) potential $V_{\rm XC}(\mathbf{x})$, defined by the equation[1]

$$V_{\rm XC}(\mathbf{x})=\frac{\delta E_{\rm XC}[n]}{\delta n(\mathbf{x})}\,, \tag{1}$$

where $E_{\rm XC}[n]$ is the XC energy functional and $n(\mathbf{x})$ is the electron number density.

In the great majority of the applications the local-density approximation (LDA) is made, in which[1]

$$E_{\rm XC}[n]=\int d^3x\, n(\mathbf{x})\varepsilon_{\rm XC}(n(\mathbf{x}))\,, \tag{2}$$

where $\varepsilon_{\rm XC}(n(\mathbf{x}))$ is the XC energy per electron in a locally uniform electron gas of density $n(\mathbf{x})$.[2] From Eqs. (1) and (2) it follows that, in LDA, $V_{\rm XC}(\mathbf{x})$ is a function of the local value of the density. By definition, the form of this function is a property of the infinite, homogeneous electron gas.

Starting with the classic work of Lang and Kohn,[3] the LDA has proved to be quite successful for many applications, such as calculations of total energies and work functions. However, recent variational calculations,[4] which do not resort to the limit of slow density variations, yield surface energies that are substantially larger than the LDA values. In addition, new experimental developments[5,6] bring to focus another limitation of the LDA: It gives rise to an XC potential that decays *exponentially* outside the surface, whereas the correct asymptotic behavior of $V_{\rm XC}(\mathbf{x})$ is that it should be *imagelike:*

$$V_{\rm XC}(\mathbf{x})\to -\frac{e^2}{4(z-z_0)}\,, \tag{3}$$

for $z>\lambda_F$ (where $\lambda_F=2\pi/k_F$, k_F being the Fermi wave vector), and z denotes the coordinate normal to the surface. The coordinate z_0 defines the position of the *effective image plane,*[3] a quantity we will discuss later on.

The determination of the potential barrier experienced by an electron in the surface region is a central question in surface physics. Renewed interest in this question originates, for example, in the experimental observation of a new class of surface states in metals,[5-7] *owing their existence* to the imagelike tail of the surface potential. The most elaborate calculations of these surface states available today[8] resort to an *ad hoc* introduction of the image behavior into $V_{\rm XC}$. In addition, the limit given by Eq. (3) is important for the evaluation of the tunnel current across the surface barrier.[9,10]

In this Rapid Communication we present the results of a first-principles calculation of $V_{\rm XC}(\mathbf{x})$ at a metal surface. In it the strongly inhomogeneous nature of the electron density at the surface is incorporated at the outset. We establish a relation between $V_{\rm XC}$ and the electron density that enables us to carry out *nonlocal* density functional calculations with the same ease as LDA-based calculations. We illustrate the method with a calculation of the position of the effective image plane.

Our procedure is an adaptation to the metal surface problem of work carried out recently in the study of the fundamental band gap of semiconductors.[11,12] It involves an interplay between many-body perturbation theory and density functional theory.

The exact electron Green's function g for a many-electron system is defined by the equation[13]

$$[E-h(\mathbf{x})]g(\mathbf{x},\mathbf{x}'|E)-\int d^3x''\Sigma_{\rm XC}(\mathbf{x},\mathbf{x}''|E)g(\mathbf{x}'',\mathbf{x}'|E)=\delta(\mathbf{x}-\mathbf{x}')\,,$$

where h is the Hartree single-electron Hamiltonian, and $\Sigma_{\rm XC}$ is the nonlocal and energy-dependent electron self-energy. One can also define a Green's function g_0 for the KS Hamiltonian, i.e.,

$$[E-h(\mathbf{x})-V_{\mathrm{XC}}(\mathbf{x})]g_0(\mathbf{x},\mathbf{x}'|E)=\delta(\mathbf{x}-\mathbf{x}')\,,$$

where $V_{\mathrm{XC}}(\mathbf{x})$ is defined by Eq. (1). Making use of the Dyson equation relating g and g_0, and of the requirement that both Green's functions give the correct electron number density, one obtains[11,12,14] the following *exact* integral equation for $V_{\mathrm{XC}}(\mathbf{x})$:

$$\int d^3x'\,V_{\mathrm{XC}}(\mathbf{x}')\int dE\,g_0(\mathbf{x},\mathbf{x}'|E)g(\mathbf{x}',\mathbf{x}|E)=\int d^3x_1\int d^3x_2\int dE\,g_0(\mathbf{x},\mathbf{x}_1|E)\Sigma_{\mathrm{XC}}(\mathbf{x}_1,\mathbf{x}_2|E)g(\mathbf{x}_2,\mathbf{x}|E)\,. \tag{4}$$

This equation, first introduced by Sham and Schlüter,[11,12] poses a self-consistency problem, since the Green's function g_0 is calculated from the knowledge of $V_{\mathrm{XC}}(\mathbf{x})$. Thus Eq. (4) is solved by iteration.

We emphasize that what is being indirectly addressed here is the nonlocality of the functional $E_{\mathrm{XC}}[n]$. The potential $V_{\mathrm{XC}}(\mathbf{x})$ is, by definition, a local potential. For the *homogeneous* electron gas, the solution of Eq. (4) is[12]

$$V_{\mathrm{XC}}=\Sigma_{\mathrm{XC}}(k=k_F;E=E_F)\,, \tag{5}$$

which is the correct local (LDA) limit.[2]

A reasonable first approximation for Σ_{XC}, which includes the important physical effect of its nonlocality, is the static Coulomb-hole plus screened-exchange (COHSEX) approximation, given by the equation[13]

$$\Sigma_{\mathrm{XC}}(\mathbf{x}_1,\mathbf{x}_2|E)\cong-\rho(\mathbf{x}_1,\mathbf{x}_2)W(\mathbf{x}_1,\mathbf{x}_2|0)+\tfrac{1}{2}[W(\mathbf{x}_1,\mathbf{x}_2|0)-v(\mathbf{x}_1-\mathbf{x}_2)]\delta(\mathbf{x}_1-\mathbf{x}_2)\,, \tag{6}$$

where ρ is the single-particle density matrix, W is the static limit of the dynamical, nonlocal, screened electron-electron interaction, and v is the bare Coulomb interaction. W is obtained from the knowledge of the density response function χ for interacting electrons.[13] In this work χ is computed using the method developed in Ref. 15.

We have solved Eq. (4) for a free-electron metal surface (jellium model). At the present time the approximation $g\cong g_0$ has been made throughout; Eq. (4) then turns into a one-dimensional integral equation of the form

$$\int dz'\,\chi^{(0)}(q_\parallel=0|zz')V_{\mathrm{XC}}(z')=F(z)\,, \tag{7}$$

where $\chi^{(0)}(q_\parallel=0|zz')$ is the two-dimensional Fourier transform of the random-phase-approximation (RPA) polarizability for zero wave vector. Equation (7) is a Fredholm integral equation of the first kind. From the numerical standpoint it defines an "ill-posed" problem:[16] Small changes in $F(z)$ can lead to large variations in the solution $V_{\mathrm{XC}}(z)$. In the surface problem this situation is further complicated by the fact that the kernel $\chi^{(0)}$ is singular.

The starting point in the iterative solution of Eq. (7) is V_{XC} in LDA. For consistency this potential is constructed in the COHSEX approximation, i.e., by using Eq. (5) in the KS equation, the bulk self-energy being evaluated in the COHSEX approximation for the local value of the density. We call this potential $V_{\mathrm{XC}}^{(0)}$. The wave functions and energy eigenvalues obtained self-consistently with $V_{\mathrm{XC}}^{(0)}$ are used in the computation of g_0, $\chi^{(0)}$, and Σ_{XC}, and Eq. (7) is solved for the first time. We call its solution $V_{\mathrm{XC}}^{(1)}$. The same is placed in the KS equation, and a new set of eigenfunctions and eigenvalues is obtained, and used to compute updated values of g_0, $\chi^{(0)}$, and Σ_{XC}. Equation (7) is solved again. We call its solution $V_{\mathrm{XC}}^{(2)}$. This procedure is repeated until convergence is achieved to a desired accuracy. We emphasize that *no approximations of a surface nature are made in this procedure.*

In Fig. 1 we give results for the case of Al ($r_s=2.07$). We show both the converged solution ($V_{\mathrm{XC}}=V_{\mathrm{XC}}^{(3)}$) and its LDA-COHSEX counterpart [$V_{\mathrm{XC}}^{(0)}=V_{\mathrm{XC}}(\mathrm{LDA})$]. The crucial difference between the "local" (i.e., LDA) and "nonlocal" results for $V_{\mathrm{XC}}(z)$ is that the latter potential is imagelike outside the surface. This represents an important improvement for problems such as the evaluation of the binding energies of image-potential bound states,[7] tunnel barriers for scanning-tunneling microscopy,[9] etc.

There has been recent controversy[17] about the effect of the inclusion of nonlocality in $E_{\mathrm{XC}}[n]$ on the calculated value of the position of the effective image plane z_0 [see Eq. (3)]. A density functional calculation by Ossicini, Bertoni, and Gies[17] predicts substantially smaller values of z_0 than the LDA results of Lang and Kohn.[3] On the

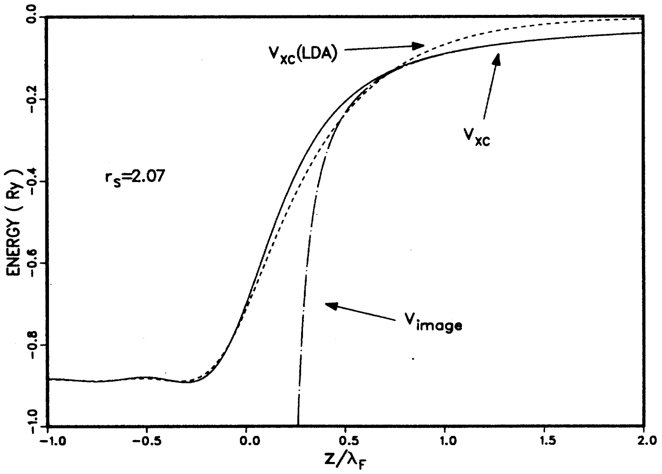

FIG. 1. Converged solution of Eq. (7), $V_{\mathrm{XC}}(z)=V_{\mathrm{XC}}^{(3)}(z)$, for $r_s=2.07$, corresponding to the bulk density of Al. The figure also shows the XC potential in LDA COHSEX, and the "classical" image potential defined by Eq. (3) for all z, for $z_0=0.63$ Å (see Table I). The coordinate z is measured from the jellium edge (in units of λ_F).

basis of a heuristic treatment of the XC hole, Serena, Soler, and Garcia[17] obtained only a slight reduction in the value of z_0 relative to the LDA result. Now, in addition to lacking full self-consistency, these papers leave the following question open. The LDA results for z_0 obtained by Lang and Kohn[3] in their seminal paper on the subject, refer to the image potential experienced by an *external, distinguishable* charge; they are obtained in the context of linear response to that charge. The question is whether the value of z_0 obtained in linear response is the same as the one that controls the image tail of $V_{\mathrm{XC}}(z)$; in other words, are there electron-overlap effects built into the value of z_0 defined by Eq. (3)? Our self-consistent solution to Eq. (7) allows us to address this question for the first time.

First we determine a value of z_0 from the image tail of $V_{\mathrm{XC}}(z)$. For all values of z outside the jellium edge we write the equation

$$V_{\mathrm{XC}}(z) = -\frac{e^2}{4[z-z_0(z)]}, \tag{8}$$

which we solve for the function $z_0(z)$. If $V_{\mathrm{XC}}(z)$ is indeed imagelike outside the surface, $z_0(z)$ must become independent of z for large z, the asymptotic value of $z_0(z)$ defining the position of the effective image plane.[18] This is illustrated in Fig. 2 for $r_s = 5.63$ (Cs), which clearly demonstrates the importance of self-consistency for extracting reliable values of z_0.

Next we determine a value of z_0 from linear response. In Fig. 3 we show our self-consistent result for V_{XC} plotted versus the electron density n for values of n ranging from zero (for the vacuum outside) to the first Friedel peak inside the jellium. We also show a similar result obtained for LDA-COHSEX. Our nonlocal result for V_{XC} (it derives implicitly from a nonlocal functional $E_{\mathrm{XC}}[n]$) was parametrized via a set of spline coefficients. This prescription for relating V_{XC} to n for every point in the surface region enables us to carry out *nonlocal density functional calculations.* (For values of z beyond the first Friedel peak we use LDA.) The KS equation was then solved self-consistently in the presence of a weak dc electric field directed along the surface normal using our nonlocal relationship between V_{XC} and n. The centroid of the induced density equals the linear-response value of z_0.[3] In order to assess the effects of nonlocality in a consistent manner, we repeated the calculation using the V_{XC} vs n relation given by LDA-COHSEX (see Fig. 3).

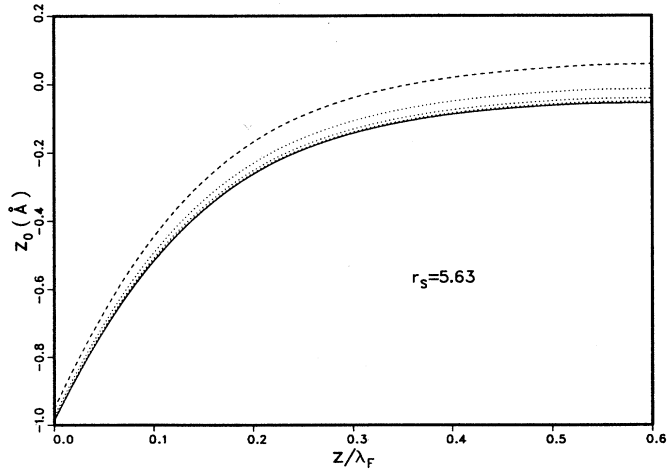

FIG. 2. Solution of Eq. (8) for $z_0(z)$ for five consecutive iterations of the solution of Eq. (7) for $r_s = 5.63$. The dashed line is obtained from $V_{\mathrm{XC}}^{(1)}$, the dotted ones from $V_{\mathrm{XC}}^{(2)}$, $V_{\mathrm{XC}}^{(3)}$, and $V_{\mathrm{XC}}^{(4)}$, respectively, and the solid one from the converged solution, $V_{\mathrm{XC}}^{(5)}$.

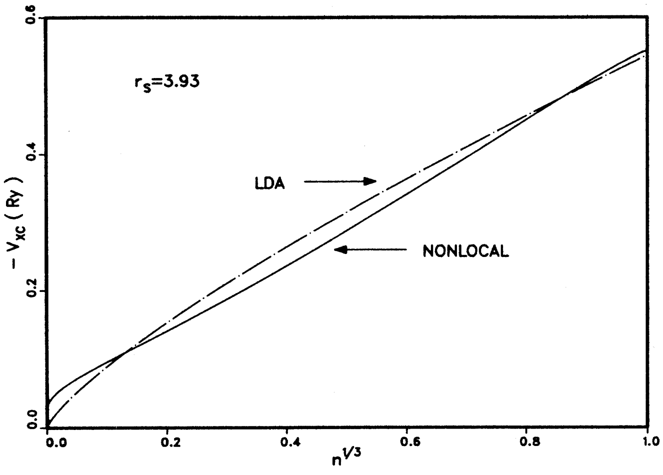

FIG. 3. "Nonlocal" relation V_{XC} vs $n^{1/3}$ for the converged solution of Eq. (7) for $r_s = 3.93$ (curve labeled "nonlocal"). The electron number density n is normalized to its value at the first Friedel peak inside the jellium; $n=0$ corresponds to the vacuum outside the surface. The "local" relation that obtains in LDA COHSEX is also shown (curve labeled "LDA").

Our results for z_0 are given in Table I. For $r_s = 2.07$ (high-density metal) the value of z_0 extracted from the image tail of $V_{\mathrm{XC}}(z)$ basically agrees with the value obtained from linear response. On the other hand, both values of z_0 *differ substantially* for intermediate and low metallic densities ($r_s = 3.93$ and 5.63, respectively). This interesting result can be understood from the fact that the work function decreases as r_s increases (i.e., as the bulk density decreases). A smaller value of the work function leads to a more pronounced tailing out (tunneling) of the electrons into the vacuum. One then expects that any electron-overlap effects built into the image tail of $V_{\mathrm{XC}}(z)$

TABLE I. Position of the effective image plane z_0, measured from the jellium edge (in a.u.), for three values of r_s. First row: result obtained from Eq. (8). Second row: result obtained from *nonlocal* linear-response theory. Third row: result obtained from linear-response theory in LDA-COHSEX.

	$r_s = 2.07$ (Al)	$r_s = 3.93$ (Na)	$r_s = 5.63$ (Cs)
From $V_{\mathrm{XC}}(z)$	1.19	0.45	−0.11
From nonlocal linear response	1.16	0.84	0.68
From local linear response (LDA COHSEX)	1.25	0.95	0.79

(i.e., into z_0) would become more significant as r_s increases, in agreement with our numerical results. That overlap effects exist at all is a consequence of the fact that the asymptotic limit given by Eq. (3) is reached rather quickly (i.e., for $z \lesssim \lambda_F$), as seen in Figs. 1 and 2.

From Table I we also have that density functional nonlocality leads to a (relatively small) *reduction* of the linear-response value of z_0. This result is not immediately obvious, since, as expected, the nonlocal image tail of $V_{\text{XC}}(z)$ has the effect of lowering the work function.[19] Its explanation resides in the fact that the density induced by a weak electric field (whose centroid defines z_0) is extremely small for the values of $z(z \sim \lambda_F)$ for which the enhanced tunneling associated with a lower work function would produce an effect opposite to the one found.

The choice of the model employed in the treatment of XC effects is an important quantitative consideration. For example, the linear-response values of z_0 obtained in LDA using KS exchange and Wigner's interpolation for correlation are (in a.u.) 1.55, 1.25, and 1.17, respectively, for the same densities for which the LDA-COHSEX results are given in the third row of Table I. The results of the present paper, based on the use of the COHSEX approximation for Σ_{XC}, establish a *qualitative benchmark* for $V_{\text{XC}}(z)$. Work is in progress in which the energy dependence of Σ_{XC} is treated in the GW approximation,[13] which has proved capable of giving accurate results for, e.g., band gaps in semiconductors.[11,14,20,21] [Equation (6) is a static approximation to the full GW self-energy.]

In conclusion, we have presented the first explicit evaluation of $V_{\text{XC}}(z)$ at a metal surface in which the strongly inhomogeneous, self-consistent electron density profile at the surface is treated from first principles. We have evaluated the position of the effective image plane z_0 via a self-consistent, nonlocal density functional calculation of the electron density induced by a dc electric field. We have also evaluated z_0 from the image tail of $V_{\text{XC}}(z)$. We attribute the difference in both values of z_0 to electron-overlap effects present in $V_{\text{XC}}(z)$.

The work of A.G.E. was supported by Montanians on a New Track for Science (MONTS) Grant No. 196754, by the National Science Foundation Grant No. DMR 86-03820, and by the San Diego Supercomputer Center.

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