PHYSICAL REVIEW B VOLUME 18, NUMBER 2 15 JULY 1978

Change-in-self-consistent-field theory of the work function

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(Received 22 February 1978)

By analogy with the change-in-self-consistent-field (ΔSCF) method of atomic physics, the work function of a metal surface is computed as the difference between the total energy of the system in its final state, where one electron is missing from the metal and removed to a large distance from the surface, and its initial state, where the metal is charge neutral. Our ΔSCF expression is a generalization of one given by Lang and Kohn, who assumed the electron density profile to be that of a jellium surface. The ΔSCF expression also reduces in the appropriate limit to an expression derived by Mahan and Schaich. We show that the ΔSCF expression is much less profile-sensitive than other exact expressions for the work function and is therefore well suited for use with approximate profiles. We apply our "variational self-consistent" profiles (more realistic than jellium profiles) to evaluate the ΔSCF work function for a few selected surfaces of simple metals, among them the three low-index faces of Al, for which agreement with experiment is found to be good.

I. INTRODUCTION

This paper is concerned with the accurate calculation of the face-dependent work function of a metal within the density-functional theory of the inhomogeneous electron gas.[1,2] The question of accuracy arises for any approximate solution of the metal-surface problem. Examples of such approximate solutions include those in which the total energy is minimized by variation of a small number of parameters,[3-5] those in which a model problem (such as the jellium surface[6]) is solved self-consistently instead of the real problem, and the "variational self-consistent" solutions we have recently proposed,[7,8] in which the model problem to be solved self-consistently is itself varied in order to minimize the energy. Each of these approximations yields an electron density profile which is *not* a self-consistent solution of the real metal surface problem.

We will present three exact density functionals [Eqs. (2.7), (2.8) and (2.13)] for the work function of a real surface which are numerically equal for a self-consistent electron density profile at the surface. For a non-self-consistent profile these three expressions can differ. We show rigorously that the least profile sensitive and therefore the most accurate expression is the ΔSCF expression [Eq. (2.13)], which takes advantage of the fact that the charge defect left behind by the escaped electron is localized at the surface of the metal in order to compute the work function as the difference between the total surface energy of the system in its final state, where one electron is missing from the metal and removed to infinity, and its initial state, where the metal is charge neutral. This is of course an extension to a macroscopic system of the ΔSCF (change in self-consistent field) method for calculating ionization energies of atoms.[9] Lang and Kohn[10] were the first to take a ΔSCF approach to calculate work functions for low-index faces of simple metals, but they assumed from the outset that the electron density profiles were close to those of the jellium surface. Since we have recently found[7,8] that the electron density profiles at the surfaces of simple metals are often *not* jelliumlike, and in fact depend strongly on the choice of exposed crystallographic face [see Fig. 1(a)], we have derived the explicit ΔSCF expression for a more general electron density profile at the surface and evaluated it for our variational self-consistent profiles.

The ΔSCF work functions we calculate agree within a few tenths of an electron volt with those of Lang and Kohn.[10] This numerical confirmation of the profile insensitivity of the ΔSCF expression suggests that the ΔSCF work functions calculated here should be highly accurate.

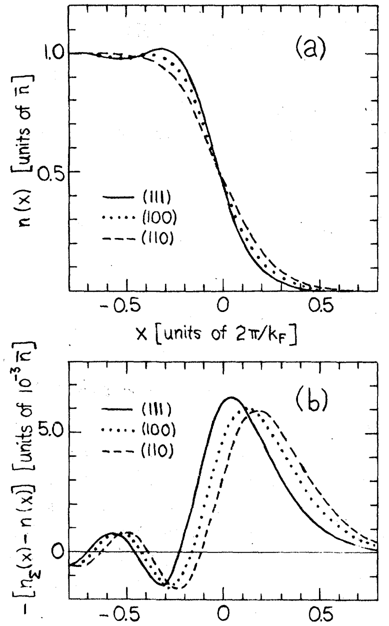

FIG. 1. (a) Face-dependent electron-density profiles $n(x)$ for the (neutral) surface of fcc Al, calculated by the variational self-consistent method using the variational form (1.12). x is the distance from the jellium edge. The profile for the (100) face is closest to the jellium profile. (b) Face dependence of the relaxed surface charge profile left behind at the Al surface by an escaped electron, calculated by the variational self-consistent method using the variational form (1.12). x, the distance from the jellium edge, is scaled as in (a) to facilitate comparison with the electron-density profiles. The centroids of the surface charge density are, respectively, at 0.16 [(111)], 0.27 [(100)], and 0.38 [(110)] Fermi wavelengths outside the jellium edge. (The curves were obtained for a total surface charge $\Sigma = 5 \times 10^{-4}$ atomic units. The Fermi wavelength of Al is 6.77 atomic units.)

On the other hand, the other two expressions for the work function considered here are found to be highly profile sensitive. One of them, called here the "out" work function, [Eq. (2.8)] gives realistic (within a few tenths of an eV) work functions when evaluated for our variational self-consistent profiles, which are therefore shown to be more realistic than the jellium profiles, which give "out" work functions in error by *several* electron volts for the metals of higher electron density.

We conclude this introduction by reviewing first the exact, self-consistent solution for the real metal surface, and then some approximate solutions.

The ground-state energy of a system of electrons interacting with static ions via a local pseudopotential $w(r)$ can be written as a functional of the electron number density $n(\vec{r})$:

$$E\{n\} = T_s\{n\} + E_{xc}\{n\} + \frac{1}{2}\int d\vec{r}\,d\vec{r}\,'\,\frac{n(\vec{r})n(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|} + \int d\vec{r}\sum_{\vec{l}} w(|\vec{r}-\vec{l}|)n(\vec{r}) + \frac{1}{2}\sum_{\vec{l},\vec{l}\,'}{}' \frac{z^2}{|\vec{l}-\vec{l}\,'|}\,. \qquad (1.1)$$

(Atomic units $\hbar = |e| = m = 1$ are used in all the equations of this paper). The first three terms of (1.1) are the noninteracting kinetic energy, exchange-correlation energy, and Hartree electrostatic energy, respectively, as defined in density-functional theory.[1,2] [Like Lang and Kohn,[6,10] we will treat the exchange-correlation energy in the "local density approximation"[2]; it has recently been shown that this approximation will produce errors in the work function of at most a few hundredths of an eV.[11] For the ionic pseudopotential $w(r)$ we will use Ashcroft's form.[12] The pseudopotential core radius, and indeed all input parameters of our calculation, will be the same as in Refs. 8 and 10.] The last term in (1.1) is the Coulomb interaction between the ions distributed over sites $\vec{l}$. The energy functional (1.1) is minimized[1] by the correct $n(\vec{r})$. The self-consistent electron density $n(\vec{r})$ is constructed from auxiliary one-electron wave functions[2] which satisfy Schrödinger's equation with the effective potential

$$v_{\text{eff}}(\{n\};\vec{r}) = \phi(\{n\};\vec{r}) + \delta v(\vec{r}) + \mu_{xc}(\{n\};\vec{r})\,, \qquad (1.2)$$

where

$$\phi(\{n\};\vec{r}) = \int d\vec{r}\,'\,\frac{n(\vec{r}\,') - n_+(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}\,, \qquad (1.3)$$

$$\delta v(\vec{r}) = \sum_{\vec{l}} w(|\vec{r}-\vec{l}|) + \int d\vec{r}\,'\,\frac{n_+(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}\,, \qquad (1.4)$$

$$\mu_{xc}(\{n\};\vec{r}) = \frac{\delta}{\delta n(\vec{r})}E_{xc}\{n\}\,. \qquad (1.5)$$

Here $n_+(\vec{r}) = \bar{n}\Theta(-x)$ is a fictitious semi-infinite uniform positive background of density equal to the bulk electron density $\bar{n}$.

The self-consistent solution of the exact one-electron Schrödinger equation is laborious, largely because of the three-dimensional spatial variation of v_{eff}, Eq. (1.2). In an approximate solution, an approximate density profile is constructed from approximate one-electron wave functions which satisfy a Schrödinger equation with $v_{\text{eff}}(\{n\};\vec{r})$ replaced by some approximation $v_{\text{eff}}^{\text{in}}(\vec{r})$ which usually varies only in the x direction (perpendicular to the surface). The "in" superscript is meant to suggest that this is the effective potential which goes *in* to the calculation of the approximate density profile $n(\vec{r})$. On the other hand, given this approximate $n(\vec{r})$, another approximation to the effective potential for the real surface would be

$$v_{\rm eff}^{\rm out}(\{n\};\vec{r}) = \phi(\{n\};\vec{r}) + \delta v(\vec{r}) + \mu_{xc}(\{n\};\vec{r}) \,, \qquad (1.6)$$

where ϕ and μ_{xc} are obtained from (1.3) and (1.5) evaluated for the approximate $n(\vec{r})$. The "out" superscript is meant to imply that this is the effective potential which comes *out* of the calculation of the approximate $n(\vec{r})$. Of course $v_{\rm eff}^{\rm out} = v_{\rm eff}^{\rm in}$ if and only if $n(\vec{r})$ happens to be the self-consistent solution of the real surface problem (1.1).

If $v_{\rm eff}^{\rm in}$ as defined above depends only on x, the distance perpendicular to the surface, then so will n, $\phi\{n\}$ and $\mu_{xc}\{n\}$ (but not δv). If in addition $v_{\rm eff}^{\rm in}$ tends to a constant as $x \to -\infty$ (deep inside the metal), then

$$n(x) = \frac{1}{\pi^2} \int_0^{k_F} dk (k_F^2 - k^2)[\psi_k(x)]^2 \,, \qquad (1.7)$$

where

$$\left(-\frac{1}{2}\frac{d^2}{dx^2} + v_{\rm eff}^{\rm in}(x)\right)\psi_k(x) = \left(\frac{k^2}{2} + v_{\rm eff}^{\rm in}(-\infty)\right)\psi_k(x) \,. \qquad (1.8)$$

As x tends to $-\infty$, $n(x)$ tends to the bulk density $\bar{n}$ and

$$\psi_k(x) \to \sin[kx - \gamma(k)] \,. \qquad (1.9)$$

We now describe some different approximate solutions which are characterized by different ways of constructing $v_{\rm eff}^{\rm in}(x)$. The simplest is the purely variational solution,[4,5] in which $v_{\rm eff}^{\rm in}(x)$ is some analytic function depending on one or more parameters which are varied to minimize the energy (1.1).

In the Lang-Kohn[6,10] approximation, which we refer to as "perturbational self-consistent," the discrete lattice perturbation $\delta v(\vec{r})$ is treated as a weak perturbation: the "jellium surface" model problem

$$v_{\rm eff}^{\rm in}(\{n\};x) = \phi(\{n\};x) + \mu_{xc}(\{n\};x) \,, \qquad (1.10)$$

which is obtained from (1.2) in the limit $\delta v(\vec{r}) \to 0$, is first solved self-consistently. Then $\delta v(\vec{r})$ is reintroduced as a first-order perturbation to the surface energy[6] and work function.[10]

The discrete-lattice potential $\delta v(\vec{r})$ is zero far outside the metal, but has for many metal surfaces a large (± several eV) average value $\langle \delta v \rangle_{av}$ inside. Consequently the jellium model profiles are unrealistic for these surfaces.[8] However the jellium model has the appealing feature that it leads to a one-dimensional problem with simple boundary conditions, which can easily be solved on a computer. Furthermore, it is known to give a reasonable description of the bulk,[8] so that one expects the presence of the surface to be the dominant source of inhomogeneity in the electron density. This led us to propose the variational self-consistent method,[7,8] which preserves the computational simplicity of the Lang-Kohn[6] approach while accounting for the presence, due to the discreteness of the ion distribution, of an additional potential in the half space occupied by the metal. Explicitly, we minimize the surface energy for a given face of a given metal over a restricted class of electron density profiles, which have the common feature that they all go to their jellium value far inside the metal. The individual profiles $n(x)$ are obtained by solving self-consistently the one-electron equations (1.7) and (1.8), with

$$v_{\rm eff}^{\rm in}(\{n\};x) = \phi(\{n\};x) + V(x) + \mu_{xc}(\{n\};x) \,, \qquad (1.11)$$

where $V(x)$ is a parametrized fictitious potential which "mocks up" $\delta v(\vec{r})$, and again ϕ and μ_{xc} are obtained from Eqs. (1.3) and (1.5) evaluated for the approximate $n(x)$. The two functional forms we considered[8] were

$$V(x) = C\Theta(-x) \qquad (1.12)$$

$$V(x) = \langle \delta v \rangle_{\rm av} \Theta(-x + X) \qquad (1.13)$$

where C and X are variational parameters and $\langle \delta v \rangle_{\rm av}$ is the (crystallographic face-dependent) average of $\delta v(\vec{r})$ over the volume of the semi-infinite crystal. Both forms gave similar results for the surface energies and density profiles; the calculated energies were lower (and sometimes significantly so) than those of Lang and Kohn, and the calculated electron density profiles were often quite different from those of the jellium surface. (Of course the Lang-Kohn[6] calculation would be recovered from (1.11) by taking $V(x) = 0$ or constant, i.e., by the special values $C = 0$ or $X = +\infty$ of the variational parameters.)

The effect of relaxation of the position of the first lattice plane after formation of the surface will be for the most part neglected here, as it was in our previous work[7,8] and that of Lang and Kohn.[6,10] We believe that lattice relaxation has little effect on the work function.[8] However, *if* such a lattice relaxation has been calculated for the neutral surface, it need not be recomputed for the charged surface (as shown in Appendix A). This latter conclusion has been reached independently by Schulte.[13]

II. THREE EXPRESSIONS FOR THE WORK FUNCTION

The work function, i.e., the minimum energy required to remove an electron from a metal at zero temperature, is known from experiment[14] and theory[10,15] to depend on the crystalline face considered. By definition

$$W = \phi(\{n\};\infty) + E_{N-1} - E_N \,, \qquad (2.1)$$

where E_N and E_{N-1} are, respectively, the ground-state energy of the metal containing N and $N-1$ electrons, the number of positive charges being N in both cases. $\phi(\{n\};\infty)$ is the electrostatic potential energy of an electron far from the (neutral) metal, its distance from the surface being large enough for it to be in the asymptotic region, but small compared with any linear dimension of the crystalline face under study. (In practice and hereinafter the work function is evaluated for a semi-infinite metal filling the half space $x<0$.)

Using the definition of the chemical potential

$$\mu = E_N - E_{N-1}\,, \tag{2.2}$$

Eq. (2.1) can be rewritten as

$$W=\phi(\{n\};\infty)-\mu\,. \tag{2.3}$$

Lang and Kohn[10] have shown that in the density-functional approach the chemical potential is given by

$$\mu=\delta E\{n\}/\delta n(\vec{r})\,, \tag{2.4}$$

where $E\{n\}$ is the exact ground-state energy (1.1) of the neutral metal. Evaluation of the functional derivative (2.4) gives

$$\mu=v_{\text{eff}}(\{n\};\vec{r})+[\delta/\delta n(\vec{r})]T_s\{n\}\,, \tag{2.5}$$

with v_{eff} given by Eq. (1.2). Since μ is a constant (independent of $\vec{r}$), we may replace it by its average value $\langle\mu\rangle_{\text{av}}$ over the volume of the semi-infinite metal:

$$\langle\mu\rangle_{\text{av}}=\langle v_{\text{eff}}\rangle_{\text{av}}+\left\langle\frac{\delta}{\delta n(\vec{r})}T_s\{n\}\right\rangle_{\text{av}}\,. \tag{2.6}$$

So far no approximation has been made. But suppose now that we have an approximate, non-self-consistent solution to the metal surface problem. Then there may be an ambiguity in the chemical potential (2.6). We may use the potential $v_{\text{eff}}^{\text{in}}$, defined in the paragraph following Eq. (1.5), which gives the "in" work function (called the "exact work function for the model problem" in our previous work[8]):

$$W_{\text{in}}=v_{\text{eff}}^{\text{in}}(\infty)-\langle v_{\text{eff}}^{\text{in}}\rangle_{\text{av}}-\left\langle\frac{\delta}{\delta n(\vec{r})}T_s\{n\}\right\rangle_{\text{av}}; \tag{2.7}$$

or we may use the potential $v_{\text{eff}}^{\text{out}}$, defined in Eq. (1.6), which gives the "out" work function (called the "variational work function"—an unsatisfactory name—in our previous work[8]):

$$W_{\text{out}}=v_{\text{eff}}^{\text{out}}(\infty)-\langle v_{\text{eff}}^{\text{out}}\rangle_{\text{av}}-\left\langle\frac{\delta}{\delta n(\vec{r})}T_s\{n\}\right\rangle_{\text{av}}\,. \tag{2.8}$$

Of course for a self-consistent solution ($v_{\text{eff}}^{\text{out}}=v_{\text{eff}}^{\text{in}}$) these two expressions become identical. They can however be very different, even for a good approximation to the electron density profile. For example, consider the purely variational "infinite linear potential model,"[5,15] in which $v_{\text{eff}}^{\text{in}}(x)$ is taken to be a constant $v_{\text{eff}}^{\text{in}}(-\infty)$ for $x<x_0$ (where x_0 is chosen to satisfy charge conservation) and $v_{\text{eff}}^{\text{in}}(-\infty)+F(x-x_0)$ for $x>x_0$. When the slope parameter F is chosen to minimize the surface energy of jellium,[5] W_{out} yields quite reasonable values for the jellium work function while W_{in} is always infinite (because $v_{\text{eff}}^{\text{in}}(+\infty)$ is]. This example shows that W_{in} is sensitive to the asymptotic decay of the electron density in the region far outside the surface, while W_{out} depends only on the overall relaxation or "spilling out" of the electron density after formation of the surface (and on bulk properties).

So long as the approximate density profile tends to a constant $\bar{n}$ as $x\to-\infty$ (i.e., deep inside the metal), the second term on the right in (2.6) becomes $\frac{1}{2}k_F^2$, where $k_F=(3\pi^2\bar{n})^{1/3}$ is the Fermi wave vector. Thus for the variational self-consistent density profiles

$$W_{\text{in}}=D_e-[\tfrac{1}{2}k_F^2+\mu_{xc}(\bar{n})+V(-\infty)]\,, \tag{2.9}$$

$$W_{\text{out}}=D_e-[\tfrac{1}{2}k_F^2+\mu_{xc}(\bar{n})+\langle\delta v\rangle_{\text{av}}]\,, \tag{2.10}$$

where

$$\begin{aligned}D_e&=\phi(\{n\};+\infty)-\phi(\{n\};-\infty)\\&=4\pi\int_{-\infty}^{\infty}dx\,x\,[n(x)-\bar{n}\Theta(-x)]\,,\end{aligned} \tag{2.11}$$

the dipole barrier due to electronic relaxation after formation of the surface, depends implicitly on $V(x)$. Here $\mu_{xc}(\bar{n})=\partial[\bar{n}\epsilon_{xc}(\bar{n})]/\partial\bar{n}$ where $\epsilon_{xc}(\bar{n})$ is the exchange-correlation energy per electron of a uniform electron gas of density $\bar{n}$. Note that the "in" (2.9) and "out" (2.10) expressions agree when $V(-\infty)=\langle\delta v\rangle_{\text{av}}$; this is guaranteed in one version of the variational self-consistent method $[V(x)=\langle\delta v\rangle_{\text{av}}\Theta(-x+X)]$ and usually turns out to be approximately true in the other $[V(x)=C\Theta(-x)]$. Note further that (2.9) and (2.10) are both exact expressions for the work function of the "model problem" in which $\delta v(\vec{r})$ is replaced by $V(x)$.

In Tables I and II we show the "in" and "out" work functions and the corresponding dipole barriers D_e for low-index faces of several simple metals, evaluated here using first the jellium model $[V(x)=0]$ electron density profiles and then the variational self-consistent profiles[8] in both versions (1.12) and (1.13) of the method. Note that the jellium model profiles, which are face independent, predict a face-independent dipole barrier and "in" work function, and an "out" work function that varies strongly (by several eV!) from face to face (due to the face dependence of $\langle\delta v\rangle_{\text{av}}$). On the other hand, the strongly face-dependent variational self-consistent profiles predict a weak face dependence for the work function, in

TABLE I. "In" and "out" work function in eV for a few selected metals and faces, calculated from Eqs. (2.9) and (2.10), respectively, using the approximate electron-density profiles of the perturbational self-consistent (PSC) scheme (i.e., the jellium surface profiles) and those of the variational self-consistent scheme in the versions of Eq. (1.12) (VSC-I) and Eq. (1.13) (VSC-II). The "in" and "out" work functions as defined in Eqs. (2.7) and (2.8) would be equal for a fully self-consistent solution of the real surface problem; note how badly this equality fails for the PSC profiles.

Metal & face		PSC		VSC-I		VSC-II
		W_{in}	W_{out}	W_{in}	W_{out}	$W_{\mathrm{in}} = W_{\mathrm{out}}$
Al fcc	(111)	3.9	5.6	4.2	4.0	4.1
	(100)	3.9	3.7	3.8	4.7	3.9
	(110)	3.9	0.9	3.7	4.5	3.8
Pb fcc	(111)	3.8	7.7	6.1	3.7	3.9
	(100)	3.8	5.7	4.4	3.8	4.0
	(110)	3.8	2.6	3.6	4.4	3.8
Zn hcp	(0001)	3.8	4.5	3.9	4.3	. . .
Mg hcp	(0001)	3.7	4.0	3.6	4.2	. . .
Na bcc	(110)	3.1	3.1	3.0	3.3	3.1
	(100)	3.1	2.2	2.8	3.0	2.9
	(111)	3.1	1.6	2.8	2.7	2.7

TABLE II. Dipole barrier D_e in eV due to electronic relaxation after formation of the surface, as defined in Eq. (2.11), calculated for the electron-density profiles of the PSC, VSC-I, and VSC-II schemes (see caption of Table I). The VSC profiles properly show a strong face dependence of D_e, while the PSC profiles do not.

Metal and face		PSC	VSC-I	VSC-II
Al	(111)	6.2	4.7	4.8
	(100)	6.2	7.2	6.4
	(110)	6.2	9.8	9.1
Pb	(111)	4.8	0.8	0.9
	(100)	4.8	2.9	3.1
	(110)	4.8	6.5	5.9
Zn	(0001)	4.8	4.6	. . .
Mg	(0001)	3.3	3.7	. . .
Na	(110)	1.0	1.2	1.0
	(100)	1.0	1.8	1.7
	(111)	1.0	2.1	2.1

agreement with all theory[10] and experiment.[14] Clearly the dipole barriers D_e of the variational self-consistent profiles are more realistic than those of jellium.

The two expressions for the work function presented so far [Eqs. (2.7) and (2.8)] involve the chemical potential μ, a bulk property. However, it is well known from elementary electrostatics that excess charge on a metal will localize at the surface. This is true in particular for the relaxed charge defect left behind by the electron in an experiment (e.g., photoemission) that measures the work function. As a result, it should be possible to compute the latter as the difference between surface-related quantities alone. This is achieved in the ΔSCF expression, our *third* exact density functional for the work function, which is obtained directly from (2.1):

$$W_{\Delta \mathrm{SCF}} = \lim_{\Sigma \to 0} \frac{1}{\Sigma A}\left(E\{n_\Sigma\} - E\{n_{\Sigma=0}\}\right), \tag{2.12}$$

where $n_\Sigma(\vec{r})$ is the electron density for a state in which Σ electrons per unit area have been carried off to rest at $x = \infty$, (these electrons still being counted in n_Σ) and the remaining electrons inside the metal have relaxed by formation of a surface charge density Σ. Since this relaxation process leaves the bulk electron density unchanged by the removal of an electron, we can write (2.12) in terms of the surface energy σ alone:

$$W_{\Delta \mathrm{SCF}} = \frac{d\sigma}{d\Sigma}\bigg|_{\Sigma=0} . \tag{2.13}$$

Since the ΔSCF expression, Eq. (2.13), may be somewhat unfamiliar, we pause here to derive from it a familiar expression[17] for the contact potential difference between two different metals. Consider a parallel plate capacitor in which the first plate has work function W_1 and is separated by a macroscopic distance D (much less than any lateral plate dimension) from the second, which has a smaller work function W_2. Let the two plates be linked by a conducting path which transfers a surface charge $-\Sigma$ to the first plate, and leaves $+\Sigma$ on the second. Only the surface energy changes in this process, and by an amount

$$(W_2 - W_1)\Sigma + \tfrac{1}{2} 4\pi D \Sigma^2 , \tag{2.14}$$

where the term linear in Σ follows from (2.13), and the quadratic term arises from the long-range electrostatic interaction between plates. Minimizing the energy with respect to Σ gives

$$4\pi \Sigma D = W_1 - W_2 \tag{2.15}$$

for the potential difference between plates, a result more conventionally derived[17] by equating the chemical potentials of the two metals.

The ΔSCF expression (2.12) or (2.13) is exact. Suppose now that we use an approximate, non-self-consistent electron density profile $n_\Sigma(\vec{r})$ to evaluate E or σ. By the variational principle,[1] the error in the energy $E\{n_\Sigma\}$ is *second-order* in the error of n_Σ. Thus we can expect $W_{\Delta\mathrm{SCF}}$, like σ, to be insensitive to the choice of density profile. $W_{\Delta\mathrm{SCF}}$ should be a highly accurate expression when the surface energies of the charged and neutral systems are obtained variationally. (In Appendix A, we show that only the ΔSCF expression avoids spurious terms that arise from use of an approximate density profile. We also show there that in variational[3-5] and variational self-consistent[8] schemes the parameters which minimize the surface energy of the neutral system suffice for the charged system as well.)

Before deriving a general explicit expression for $W_{\Delta\mathrm{SCF}}$, we note that it must take a particularly simple form in perturbational[6,10] and variational[8] self-consistent schemes. In these schemes we solve exactly and self-consistently the problem in which the discrete-lattice perturbation $\delta v(\vec{r})$ [Eq. (1.4)] is replaced by a model potential $V(x)$ [Eqs. (1.12) and (1.13)], and we then reintroduce $\delta v(\vec{r}) - V(x)$ as a weak first-order perturbation. Since W_{in} is the work function to zeroth order in $\delta v(\vec{r}) - V(x)$, Eq. (2.13) evaluated to first order in $\delta v(\vec{r}) - V(x)$ is just

$$W_{\Delta\mathrm{SCF}} = W_{\mathrm{in}} + \int_{-\infty}^{\infty} dx\, [\delta v(x) - V(x)] \frac{\partial}{\partial \Sigma} n_\Sigma(x) \Big|_{\Sigma=0}, \tag{2.16}$$

where $\delta v(x)$ is the planar average of $\delta v(\vec{r})$ and $n_\Sigma(x)$ is calculated self-consistently in the presence of the potential $V(x)$. [$\partial n_\Sigma(x)/\partial\Sigma$ calculated here for three faces of Al is displayed in Fig. 1b.] In the perturbational self-consistent scheme,[6,10] where $V(x) = 0$ and W_{in} is the jellium work function, [i.e., Eq. (2.9) evaluated for the jellium surface], equation (2.16) reduces to the one given by Lang and Kohn.[10]

It is also of some interest to note that the ΔSCF work function includes all the physics of the "out" work function plus electronic relaxation effects (after removal of an electron) that are neglected in W_{out}. Thus if $n_\Sigma(x) - n_{\Sigma=0}(x)$ is replaced by its unrelaxed value, $-(\Sigma A)/\Omega$ almost everywhere inside the metal and $\Sigma\delta(x-\infty)$ outside, where A is the surface area and Ω the volume of the metal, then Eq. (2.16) reduces to the "out" expression

$$W_{\mathrm{in}} - \langle \delta v \rangle_{\mathrm{av}} + \langle V \rangle_{\mathrm{av}} = W_{\mathrm{out}}\,. \tag{2.17}$$

It may seem strange that the "out" expression (2.8), which neglects electronic relaxation after removal of an electron, is still an exact density-functional for the work function. In Appendix B, we show that corrections to (2.8) are first order in this relaxation when an approximate density profile is used, but second order when the exact profile is used. These second-order corrections to "Koopmans' theorem"[18] vanish as the volume of the system becomes infinite.

III. EXPLICIT ΔSCF EXPRESSIONS

While equation (2.16) would suffice for the actual ΔSCF work-function calculations in this paper, we derive here a general explicit expression for $W_{\Delta\mathrm{SCF}}$ that can be used with, e.g., a purely variational density profile.[3-5] (We will assume that the electron density depends only on x, the distance perpendicular to the surface, and tends to a constant $\bar{n}$ as $x \to -\infty$.)

In order to evaluate (2.13), we first decompose the surface energy[8,10] [the surface piece of (1.1)]

$$\sigma\{n_\Sigma\} = \sigma_s + \sigma_{xc} + \sigma_{\mathrm{es}} + \sigma_{\mathrm{ps}} + \sigma_R + \sigma_{\mathrm{cl}} \tag{3.1}$$

and the work function

$$W_{\Delta\mathrm{SCF}} = W_s + W_{xc} + W_{\mathrm{es}} + W_{\mathrm{ps}} \tag{3.2}$$

into kinetic, exchange-correlation, electrostatic, and pseudopotential contributions. The last two terms in (3.1) are profile-independent terms (see Ref. 8) which do not contribute to the work function. Each term in the work function is the derivative with respect to the surface charge density Σ of the corresponding term in the surface energy, e.g.,

$$W_s = \lim_{\Sigma\to 0} \frac{1}{\Sigma}\left(\sigma_s\{n_\Sigma\} - \sigma_s\{n_{\Sigma=0}\}\right). \tag{3.3}$$

Let us write

$$n_\Sigma(x) = n'_\Sigma(x) + \Sigma\delta(x-\infty)\,, \tag{3.4}$$

where the first term on the right counts all the electrons which remain behind in the metal and the second term counts the electrons that have escaped to $x = \infty$. The pseudopotential contribution and the local density approximation to the exchange-correlation contribution to the surface energy are easily found as functionals of n'_Σ:

$$\sigma_{\mathrm{ps}} = \int_{-\infty}^{\infty} dx\, \delta v(x)[n'_\Sigma(x) - \bar{n}\Theta(-x)]\,, \tag{3.5}$$

$$\sigma_{xc} = \int_{-\infty}^{\infty} dx\, [n'_\Sigma(x)\epsilon_{xc}(n'_\Sigma(x)) - \bar{n}\epsilon_{xc}(\bar{n})\Theta(-x)]\,. \tag{3.6}$$

The electrostatic energy

$$\sigma_{\mathrm{es}} = \frac{1}{2}\int_{-\infty}^{\infty} dx\, \phi(\{n_\Sigma\};x)[n_\Sigma(x) - \bar{n}\Theta(-x)] \tag{3.7}$$

becomes, to first order in Σ,

$$\sigma_{\mathrm{es}} = \frac{1}{2}\int_{-\infty}^{\infty} dx\, \phi(\{n_\Sigma\};x)[n'_\Sigma(x) - \bar{n}\Theta(-x)] + \tfrac{1}{2}\Sigma\phi(\{n_{\Sigma=0}\};\infty)\,. \tag{3.8}$$

The surface kinetic energy is evaluated in Appendix C, with the result

$$\sigma_s = \frac{1}{2\pi^2}\int_0^{k_F} dk\, k(k_F^2 - k^2)\left(\frac{\pi}{4} - \gamma_\Sigma(k)\right) - \int_{-\infty}^{\infty} dx\, [v_{\mathrm{eff}}^{\Sigma,\mathrm{in}}(x) - v_{\mathrm{eff}}^{\Sigma,\mathrm{in}}(-\infty)]n'_\Sigma(x) - \Sigma\tfrac{1}{2}k_F^2\,, \tag{3.9}$$

where k_F is the Fermi wave vector (independent of Σ) and $\gamma_\Sigma(k)$ is the phase shift of Eq. (1.9). Of course for the neutral surface ($\Sigma = 0$), these expressions for σ reduce to those given by Lang and Kohn.[6] The Sugiyama-Langreth phase shift sum rule[19] for the case of a charged surface

$$\frac{1}{\pi^2}\int_0^{k_F} dk\, k\left(\frac{\pi}{4} - \gamma_\Sigma(k)\right) = \Sigma\,, \tag{3.10}$$

can be used to simplify (3.9):

$$\sigma_s = \frac{1}{2\pi^2}\int_0^{k_F} dk\, k^3\left(\gamma_\Sigma(k) - \frac{\pi}{4}\right) - \int_{-\infty}^{\infty} dx\, [v_{\mathrm{eff}}^{\Sigma,\mathrm{in}}(x) - v_{\mathrm{eff}}^{\Sigma,\mathrm{in}}(-\infty)]n'_\Sigma(x)\,, \tag{3.11}$$

As a first test of these expressions and of our numerics, we evaluated the ΔSCF expression (3.2) for the self-consistent electron-density profiles of the jellium surface. Here the resulting work functions should be exact (within the local density approximation) and identical to the "in" and "out" work functions of Sec. II. The work functions for jellium given by these different methods are compared in Table III, and the agreement is seen to be satisfactory. (The small discrepancies between $W_{\Delta\mathrm{SCF}}$ and $W_{\mathrm{in}} = W_{\mathrm{out}}$ are presumably due to numerical error in the evaluation of $W_{\Delta\mathrm{SCF}}$.

As a further test of the numerics, we attempted to reproduce Lang and Kohn's perturbational self-consistent calculation[10] of the work function for Al, Li, and Na, i.e., we evaluated

$$W_{\mathrm{ps}} = \int_{-\infty}^{\infty} dx\, \delta v(x) \left.\frac{\partial n_\Sigma(x)}{\partial \Sigma}\right|_{\Sigma=0} \tag{3.12}$$

using the jellium profiles for $n_\Sigma(x)$. As shown in Table IV, our values of W_{ps} so calculated are usually quite close to those of Lang and Kohn; the reason for the 0.1 eV discrepancies for Al(100), Li(111), and Na(111) are not known.[20]

We close this section by observing that the rather complicated ΔSCF expression (3.1) can be used to derive a much simpler expression which is actually a *fourth* exact density-functional for the work function. The derivation is deferred to Appendix D. The result is a simple generalization to real metals of an expression first discovered for the jellium work function by Mahan and Schaich.[21] When evaluated for approximate density profiles, this fourth expression appears to give good results for the work function, although it does not in general satisfy the kind of accuracy theorem (Appendix A) that the ΔSCF expression satisfies.

TABLE III. Work functions in eV calculated self-consistently for the *jellium surface* by the "in" and "out" expressions (2.7) and (2.8), and by the ΔSCF expression (2.13). The small discrepancies are due to numerical error in the ΔSCF calculation. r_s is the bulk density parameter $[\bar{n} = (\frac{3}{4}\pi r_s^3)^{-1}]$. The individual components of $W_{\Delta\mathrm{SCF}}$ are also shown.

r_s	$W_{\mathrm{in}} = W_{\mathrm{out}}$	$W_{\Delta\mathrm{SCF}}$	W_s	W_{xc}	W_{es}
2.07	3.88	3.95	-2.42	4.98	1.38
3.28	3.40	3.41	-1.21	3.83	0.80
3.99	3.10	3.08	-0.91	3.38	0.60

IV. NUMERICAL RESULTS AND DISCUSSION

We have calculated the ΔSCF work functions for a few selected metals and faces, using the variational self-consistent[8] electron-density profiles obtained with the form $V(x) = C\Theta(-x)$. (The step height C for the neutral metal is given in Ref. 8; we show in Appendix A that this value suffices also for the charged metal.) The expression actually evaluated here was (3.2) and not (2.16). The electron density and surface energy were evaluated for $\Sigma = 0$ and for two small nonzero values of the surface charge Σ, and the derivatives such as

TABLE IV. Pseudopotential contribution W_{ps} in eV to the ΔSCF work function, as calculated in the perturbational self-consistent scheme here and by Lang and Kohn (Ref. 10). The 0.1 eV discrepancies for Li (111) and Na (111) are not understood.

r_s	Metal and face		This work	Lang-Kohn
2.07	Al	(111)	0.18	0.19
		(100)	0.40	0.32
		(110).	-0.19	-0.21
3.28	Li	(110)	0.19	0.19
		(100)	-0.05	-0.05
		(111)	-0.24	-0.13
3.99	Na	(110)	0.01	0.03
		(100)	-0.29	-0.29
		(111)	-0.47	-0.39

TABLE V. Individual components in eV of the ΔSCF work function calculated for three faces of Al in the variational self-consistent (VSC-I) scheme.

Face	W_s	W_{xc}	W_{es}	W_{ps}	$W_{\Delta\mathrm{SCF}}$
(111)	−3.05	5.39	1.53	0.38	4.27
(100)	−2.14	4.79	1.27	0.33	4.25
(110)	−1.74	4.48	0.93	0.33	4.02

(3.3) were evaluated numerically and the results extrapolated to $\Sigma = 0$. The electrostatic potential $\phi(\{n_\Sigma\};x)$ was obtained as the solution of an integral equation[8,22] subject to the boundary condition that the slope of ϕ at large x is $4\pi\Sigma$. The various contributions to $W_{\Delta\mathrm{SCF}}$ calculated for the three faces of Al are displayed in Table V.

Of all the real metals we considered, the one which provides the most clear-cut test of our ΔSCF method is Al, for which (i) the work function has been measured for all three faces,[14,23] (ii) the Ashcroft pseudopotential is known to be quite trustworthy,[8] and (iii) the relaxation of the first lattice plane is thought to be small, at least for the (111) and (100) faces,[24,25] although for the (110) face the analysis of LEED data suggests a 10% contraction of the outer-layer spacing.[24,25] In Table VI we compare our ΔSCF results for Al with experiment[14,23] and with other theoretical calculations.[10,26-28] Of the two experiments quoted, only that of Ref. 14 monitored the cleanliness of the surface during the measurement, so that the corresponding numbers are probably more reliable than those of Ref. 23. Our results for the work function are in excellent agreement with experiment[14] for the (111) face, and too low by 0.15 eV for the (100) face and 0.25 eV for the (110) face. For this (110) face our result appears to be markedly closer to experiment than that of Lang and Kohn,[10] which is too low by 0.6 eV. [The experimental value for the (110) face may be somewhat too large due to imperfect ordering of the (110) face,[14] which tends to develop (111) facets.[25] This possibility is also supported by the fact that the polycrystalline value for the work function (4.19 eV)[10] is smaller than any of the single-crystal values of Ref. 14). On the other hand, our calculations do not show the anomalous trend[29] $W[(100)] > W[(111)]$ observed in the measurement of Ref. 14 and in the calculations of Lang and Kohn.[10]

TABLE VI. Experimental and theoretical work functions in eV for the three low index planes of Al. The Lang-Kohn values are from Ref. 10.

	(111)	(100)	(110)
Experiment:			
Ref. 14	4.24 ± 0.02	4.41 ± 0.03	4.28 ± 0.02
Ref. 23	4.26 ± 0.03	4.20 ± 0.03	4.06 ± 0.03
Theory:			
This work	4.27	4.25	4.02
Lang-Kohn	4.05	4.20	3.65
Ref. 26	...	4.49	...
Ref. 27	4.26	...	4.83*
Ref. 28	5.17	...	...

*Includes relaxation of first lattice plane.

TABLE VII. Work functions in eV for a few selected metals and faces, calculated from the ΔSCF expression by Lang and Kohn (Ref. 10) using the perturbational self-consistent profiles and calculated here using the variational self-consistent (VSC-I) profiles. The experimental polycrystalline work functions (as quoted in Ref. 10) are also shown. For single-crystalline Na (110), the experimental work function is 2.90 ± 0.10 eV (Ref. 30).

Metal and face		Lang-Kohn	This work	(Polycrystalline) Experiment
Pb	(111)	3.85	...	
	(100)	3.95	4.10	4.01
	(110)	3.80	3.90	
Zn	(0001)	4.15	4.30	4.33
Mg	(0001)	4.05	4.18	3.66
Na	(110)	3.10	3.13	
	(100)	2.75	2.84	2.7
	(111)	2.65	2.76	

The ΔSCF work functions we have calculated for Pb, Zn, Mg, and Na in the variational self-consistent scheme[8] are displayed in Table VII, where they are also compared with the work functions calculated by Lang and Kohn[10] in the perturbational self-consistent scheme (and with some experimental values.)[10,30] Although the electron-density profiles are quite different in the variational self-consistent and perturbational self-consistent schemes, the ΔSCF work functions for the two schemes usually agree within about 0.1 eV. This clearly shows the profile-insensitivity and hence the potential high accuracy of the ΔSCF method.

ACKNOWLEDGMENTS

We are grateful to N. D. Lang for helpful discussions and correspondence on several occasions during the course of this work, and to the faculty and staff of NORDITA, whose hospitality made this collaboration possible. One of us (R.M.) was supported in part by the Fonds National Suisse de la Recherche Scientifique. Two of us (J.P.P. and D.C.L.) were supported in part by NSF Grant Nos. DMR 77-08694 and DMR 75-09804. One of us (J.W.W.) was supported in part by the NSF through the Materials Science Center at Cornell University.

APPENDIX A: WHY THE VARIATIONAL PARAMETER NEED NOT DEPEND ON THE SURFACE CHARGE

Consider the surface energy $\sigma(\Sigma, C, D)$ which is a function of the surface charge density Σ and all possible variational parameters controlling the shape of the electron-density profile (and possibly also the positions of the first lattice planes), which we denote by C and D. Let C_Σ and D_Σ be the minimizing values at surface charge Σ. Then Eq. (2.13) gives the exact work function

$$W=\frac{d\sigma}{d\Sigma}(\Sigma,C_\Sigma,D_\Sigma)\bigg|_{\Sigma=0}=\frac{\partial\sigma}{\partial\Sigma}\bigg|_{\Sigma=0}+\frac{\partial\sigma}{\partial C}\frac{dC}{d\Sigma}\bigg|_{\Sigma=0}+\frac{\partial\sigma}{\partial D}\frac{dD}{d\Sigma}\bigg|_{\Sigma=0}. \tag{A1}$$

Since the variational principle guarantees that

$$\frac{\partial\sigma}{\partial C}\bigg|_{\Sigma=0}=\frac{\partial\sigma}{\partial D}\bigg|_{\Sigma=0}=0\,, \tag{A2}$$

Eq. (A1) becomes

$$W=\frac{\partial}{\partial\Sigma}\sigma(\Sigma,C_0,D_0)\bigg|_{\Sigma=0}, \tag{A3}$$

an exact relationship.

Next consider the ΔSCF approach actually employed in this paper, in which some of the variational parameters (called C) are adjusted to minimize the surface energy of the neutral metal (i.e., $\partial\sigma/\partial C\,|_{\Sigma=0}=0$), and the other variational parameters (called D), which are implicit in the choice of a particular variational form for the density profile, are kept the same for the charged as for the neutral metal (i.e., $dD/d\Sigma=0$). Once again (A1) reduces to (A3), except that now D_0 in (A3) is replaced by D (independent of Σ). It follows that in the evaluation of the ΔSCF expression (2.13), the variational parameters C_0 which minimize the surface energy for the neutral metal suffice also for the charged metal.

Finally, we note that both the "out" expression [see Eqs. (2.10) and (2.17)] and the "displaced-profile" expression (Appendix D) for the work function can be obtained from the ΔSCF expression (2.13) by suitable choices of density profile for the charged metal. These choices normally correspond to changing the parameters D (those not used to minimize σ), so for these expressions Eq. (A1) becomes

$$W=\frac{\partial\sigma}{\partial\Sigma}\bigg|_{\Sigma=0}+\frac{\partial\sigma}{\partial D}\frac{dD}{d\Sigma}\bigg|_{\Sigma=0}; \tag{A4}$$

the second term on the right-hand side is spurious, and does not arise in the full ΔSCF expression (A3).

APPENDIX B: ELECTRONIC-RELAXATION CORRECTIONS TO KOOPMANS' THEOREM

Koopmans[18] used the stationary property of the Hartree-Fock total energy to show that the ionization energy of an atom could be approximated by the negative of the highest occupied single-electron energy, with an error that goes like the *square* of the correction to the single-electron wave functions due to the electronic relaxation following ionization. There have been a number of proofs[8,31,32] that a generalized Koopmans' theorem is exact for the metal surface, i.e., that the chemical potential μ of Eq. (2.3) is also the highest occupied eigenvalue of the one-electron Schrödinger equation in the effective potential (1.2).

Suppose first that we know the exact, self-consistent one-electron wave functions $\{\psi_i\}$ for the real surface problem. Imagine removing an electron from the metal in two steps: In the first step, the electron in the highest occupied state ψ_i is removed *without* any change in the remaining wave functions, i.e., the electron density in the metal changes from $n(\vec{r})$ to $n_{\text{unrel}}(\vec{r})=n(\vec{r})-|\psi_i(\vec{r})|^2$, and the total energy changes by

$$E_{N-1}\{n_{\text{unrel}}\}-E_N\{n\}=-\langle\psi_i|h|\psi_i\rangle=-\epsilon_i\,, \tag{B1}$$

where ϵ_i is the highest occupied single-electron eigenvalue for the neutral metal. In the second step, the remaining occupied one-electron wave functions adjust to "relaxed" values, and the density relaxes to $n_{\text{rel}}(\vec{r})$. Now by the variational principle $n_{\text{rel}}(\vec{r})$ minimizes $E_{N-1}\{n\}$, i.e.,

$$E_{N-1}\{n_{\text{unrel}}\}=E_{N-1}\{n_{\text{rel}}\}+O((n_{\text{unrel}}-n_{\text{rel}})^2)\,. \tag{B2}$$

Thus the relaxation correction to the chemical potential (2.2) is of the order of the *square* of the relaxation correction to the density (integrated over the volume of the system). But the relaxation correction to the density is just to take one electronic charge away from the surface region and spread it over the bulk of the metal, in order to produce a neutral bulk and a net surface charge. Thus the relaxation correction to the density goes like the inverse of the volume of the metal in the bulk, and like the inverse of the surface area at the surface, and consequently the relaxation correction to (B2) and to the chemical potential vanishes as the volume of the system tends to infinity.

Suppose now that instead of the exact single-electron wave functions and electron densities we only have approximate ones. Then our relaxed density $n_{\rm rel}$ does *not* correspond to a minimum in E_{N-1} with respect to all possible density variations, and instead of (B2) we now have corrections to E_{N-1} that are *first-order* in the relaxation correction to the density. These corrections do not vanish as the volume tends to infinity. A perfect illustration is provided by Eq. (2.16), in which $\partial n_\Sigma(x)/\partial\Sigma$ contains significant first-order relaxation corrections.

APPENDIX C: KINETIC ENERGY CONTRIBUTION TO ΔSCF WORK FUNCTION

Our arguments here for the kinetic energy (3.9) of the charged surface are patterned after those of Huntington[33] and Lang[34] for the neutral surface. We consider a large slab of metal of thickness L, with electron density variation only perpendicular to the two faces, each of area A, at $x=0$ and $x=-L$, with a surface charge Σ on each face. The total kinetic energy is

$$T_s\{n_\Sigma\}=\sum_{i=1}^{N_\Sigma}\epsilon_i^\Sigma-2A\int_{-L/2}^{\infty}dx\,v_{\rm eff}^\Sigma(x)n_\Sigma'(x),\tag{C1}$$

where ϵ_i^Σ, the ith eigenvalue of (1.8) in the presence of the potential $v_{\rm eff}^\Sigma(x)$, includes contributions $O(1/L)$. $n_\Sigma'(x)$ is the electron density (not counting the electrons that were removed from the metal), and

$$N_\Sigma=A\int_{-\infty}^{\infty}dx\,n_\Sigma'(x).\tag{C2}$$

The surface kinetic energy is obtained by subtracting from T_s the kinetic energy of $N_{\Sigma=0}$ *bulk* electrons, i.e.,

$$\begin{aligned}\sigma_s\{n_\Sigma\}=&\frac{1}{2A}\left(\sum_{i=1}^{N_\Sigma}\epsilon_i^\Sigma-\sum_{i=1}^{N_{\Sigma=0}}\epsilon_i^{\rm bulk}\right)\\&-\int_{-L/2}^{\infty}dx\,v_{\rm eff}^\Sigma(x)n_\Sigma'(x)\\&+\int_{-L/2}^{\infty}dx\,v_{\rm eff}^{\Sigma=0}(-L/2)\bar{n}\theta(-x).\end{aligned}\tag{C3}$$

In the limit of large L, the "escaped" electrons all come from the Fermi surface,

$$\sum_{i=1}^{N_\Sigma}\epsilon_i^\Sigma=\sum_{i=1}^{N_{\Sigma=0}}\epsilon_i^\Sigma-(N_\Sigma-N_{\Sigma=0})\left[\tfrac{1}{2}k_F^2+v_{\rm eff}^\Sigma(-\tfrac{1}{2}L)\right].\tag{C4}$$

Since

$$N_\Sigma-N_{\Sigma=0}=-2\Sigma A,\tag{C5}$$

$$\int_{-L/2}^{\infty}dx\,\bar{n}\theta(-x)=\int_{-L/2}^{\infty}dx\,n_\Sigma'(x)-\frac{1}{2A}(N_\Sigma-N_{\Sigma=0}),\tag{C6}$$

and

$$v_{\rm eff}^\Sigma(-\tfrac{1}{2}L)=v_{\rm eff}^{\Sigma=0}(-\tfrac{1}{2}L),\tag{C7}$$

we get

$$\begin{aligned}\sigma_s\{n_\Sigma\}=&\frac{1}{2A}\sum_{i=1}^{N_{\Sigma=0}}(\epsilon_i^\Sigma-\epsilon_i^{\rm bulk})\\&-\int_{-L/2}^{\infty}dx\,[v_{\rm eff}^\Sigma(x)-v_{\rm eff}^\Sigma(-\tfrac{1}{2}L)]n_\Sigma'(x)-\Sigma\tfrac{1}{2}k_F^2.\end{aligned}\tag{C8}$$

Now let $L\to-\infty$ and evaluate the first term in (C8) by the method of Huntington[33] in terms of the one-electron phase shifts. The result is (3.9).

APPENDIX D: THE "DISPLACED-PROFILE" EXPRESSION

We derive here the fourth exact density functional for the work function, as promised at the end of Sec. III. Notation is as in Sec. III.

We showed in Appendix A that, in the ΔSCF expression (2.13), the variational parameters that minimize the surface energy for the neutral surface ($\Sigma=0$) may also be used for the charged surface. It follows that, in the ΔSCF expression, the density profile n_Σ' for the charged surface may be replaced by the *exact* electron-density profile $n_{\Sigma=0}$ of the neutral surface, rigidly displaced inward by a distance $-\Sigma/\bar{n}$ with respect to the positive background. The resulting expression is called the "displaced-profile" expression for the work function.

We now evaluate this expression for an approximate profile $n_{\Sigma=0}(x)$, i.e., we use

$$n_\Sigma'(x)\to n_{\Sigma=0}(x+\Sigma/\bar{n}).\tag{D1}$$

It follows immediately that

$$\frac{\partial}{\partial\Sigma}n_\Sigma'(x)\bigg|_{\Sigma=0}=\frac{1}{\bar{n}}\frac{d}{dx}n_{\Sigma=0}(x),\tag{D2}$$

$$v_{\rm eff}^{\Sigma,\rm in}(x)=v_{\rm eff}^{\Sigma,\rm in}\left(x+\frac{\Sigma}{\bar{n}}\right),\tag{D3}$$

$$\gamma^\Sigma(k)=\gamma^{\Sigma=0}(k)-k\frac{\Sigma}{\bar{n}},\tag{D4}$$

and to first order in Σ

$$\phi(\{n_\Sigma\};x)=\phi(\{n_{\Sigma=0}\};x+\Sigma/\bar{n})+4\pi\Sigma x\,\theta(x).\tag{D5}$$

Use of (D2)–(D5) to evaluate the derivatives with respect to Σ of (3.5)–(3.11) gives the simple results

$$W_s = -\tfrac{3}{5}(\tfrac{1}{2}k_F^2), \tag{D6}$$

$$W_{xc} = -\epsilon_{xc}(\bar{n}), \tag{D7}$$

$$W_{\mathrm{es}} = \phi(\{n_{\Sigma=0}\};\infty) - \phi(\{n_{\Sigma=0}\};0), \tag{D8}$$

$$W_{\mathrm{ps}} = \int_{-\infty}^{\infty} dx\, \delta(x)\, \frac{1}{\bar{n}}\, \frac{d}{dx}\, n_{\Sigma=0}(x). \tag{D9}$$

While the individual terms (D6)–(D9) will not be accurate, the work function, which is the sum of these four terms, *will* be accurate if $n_{\Sigma=0}(x)$ is a good approximation to the electron-density profile of the neutral surface [and will be exact if $n_{\Sigma=0}(x)$ is].

Note that for the jellium surface only the first 3 terms (D6)–(D8) survive. In this case we recover an exact expression for the jellium work function first derived by Mahan and Schaich.[21]

If $n_{\Sigma=0}(x)$ is a variational density profile, then the argument of Appendix A shows that in most cases the "displaced-profile" expression will introduce spurious terms into the work function—terms which are absent in the full ΔSCF expression. These spurious terms will be absent from the "displaced-profile" expression only if the rigid displacement (D1) occurs without any change in the parameters (called D in Appendix A) which specify the class of density profiles over which the energy is minimized. (This actually happens in the linear potential model[5,16]—but not in the variational self-consistent method.)[8]

The accuracy and utility of the "displaced-profile" expression are now being tested by V. Sahni, J. P. Perdew, and R. Monnier.

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