PHYSICAL REVIEW B VOLUME 36, NUMBER 3 15 JULY 1987-II

Metallic surfaces in the Thomas–Fermi–von Weizsäcker approach: Self-consistent solution

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(Received 17 November 1986)

The problem of a metallic surface is studied and solved in the Thomas–Fermi–von Weizsäcker approach. The analysis of the asymptotic solutions shows that the electronic density $n(x)$ approaches its bulk value n_0 in the metal interior exponentially, oscillating about it. This behavior is found to be an effect of the von Weizsäcker term, rather than of the exchange-correlation interaction, as one may have thought. The Euler equation is solved for a slab geometry, calculating work functions and surface energies of several simple metals. The case of the pseudojellium model, recently introduced, is also considered here. The results are compared with those of the exact Lang-Kohn theory and with those of Smith.

INTRODUCTION

The problem of a metallic surface has been studied using a variety of approaches over the years. The progress that we have witnessed in recent years has been made largely possible by the density-functional theory[1,2] (DFT). In considering a given problem within the DFT, one can choose to solve the Kohn-Sham equations for the system, an approach that was pioneered by Lang and Kohn[3] for metallic surfaces. The other approach available consists in solving the Euler equation for the electronic density. In the last case one needs to have accurate expressions for the kinetic-energy functional. An alternative method has been to use the variational principle; for the problem of metallic surfaces this was first done by Smith,[4] who minimized the energy with respect to variations of the electronic density within a one-parameter family of functions. The Euler equation was solved by Warner[5] for a cesium slab. However, his discussion of this subject was incomplete, and has remained unnoticed by most workers in the field. This work is organized as follows. In Sec. I the mathematical problem is set up, and some exact results concerning the nature of the asymptotic solutions are discussed. Section II is devoted to the discussion of the numerical approach, boundary conditions, and stability. Numerical results are presented and discussed in Sec. III.

I. STATEMENT OF THE PROBLEM

Consider the jellium model of a metallic surface. The energy functional is

$$E[n]=T_s[n]+E_{\mathrm{xc}}+\tfrac{1}{2}\int \phi(x)[n(x)-n_+(x)]dx \ . \tag{1}$$

Here $n(x)$ is the electronic density and $n_+(x)$ denotes the density of the ionic background. The kinetic-energy functional is taken as the Thomas-Fermi term plus the first gradient correction (the von Weizsäcker term),

$$T_s[n]=\int [3(3\pi^2 n)^{2/3}10+\lambda(dn/ndx)^2/8]n\,dx \tag{2}$$

with $\lambda=\frac{1}{9}$. The exchange-correlation energy $E_{\mathrm{xc}}[n]$ is, in the local-density approximation (LDA),

$$E_{\mathrm{xc}}[n]=\int n(x)\varepsilon_{\mathrm{xc}}(n)dx \ . \tag{3}$$

Here $\varepsilon_{\mathrm{xc}}(n)$ is given by the Wigner interpolation formula (in atomic units),

$$\varepsilon_{\mathrm{xc}}(n)=-0.458/r_s-0.440/(7.8+r_s) \ . \tag{4}$$

The last term in (1) represents the electrostatic energy of the system, where $\phi(x)$ satisfies Poisson's equation,

$$\frac{d^2\phi}{dx^2}=4\pi[n_+(x)-n(x)] \ . \tag{5}$$

To solve the minimization problem posed by the functional (1), write the Euler equation,

$$(\lambda/4)[d(dn/n\,dx)/dx+\tfrac{1}{2}(dn/n\,dx)^2] =\tfrac{1}{2}(3\pi^2 n)^{2/3}+V_{\mathrm{xc}}(n)+\phi(x)-\mu \ . \tag{6}$$

It is convenient to write this equation in terms of the new independent variable $u(x)=[n(x)]^{1/2}$,

$$(\lambda/2)d^2u(x)/dx^2=[\tfrac{1}{2}(3\pi^2 n)^{2/3}+V_{\mathrm{xc}}(n) +\phi(x)-\mu]u(x) \ . \tag{7}$$

Consider now the semi-infinite metal, then $n_+(x)$ is

$$n_+(x)=n_0\Theta(-x) \ . \tag{8}$$

Here n_0 is the bulk density of the metal.

Now study the asymptotic behavior of the solution, both inside and outside the metal. First, discuss the behavior outside the metal. From Eq. (6) it is seen that if one assumes that $n(x)=Ae^{-\omega x}$ for large $x>0$, then

$$(\lambda/8)\omega^2=\phi(\infty)-\mu=\Phi \ , \tag{9}$$

where Φ is the work function and where charge neutrality has been assumed. Note that the exact solution $u(x)$ has a behavior that differs from the behavior of the Thomas-Fermi solution, which decays only with a power law. Mathematically, this is due to the fact that the gradient correction is a singular perturbation term; each new gradient correction term adds higher-order derivatives to the corresponding Euler equation.

In the metal interior $n(x)$ must approach n_0; therefore, we write $n(x)=n_0(1+Q)$, and linearize Eqs. (6) and (7), obtaining

$$(\lambda/4)d^2Q/dx^2=\alpha Q+\phi-\mu \ , \tag{10a}$$

$$\frac{d^2\phi}{dx^2}=-\beta Q \ , \tag{10b}$$

where the constants α and β are given by

$$\alpha=\tfrac{1}{3}k_f^2+n_0 dV_{\mathrm{xc}}(n_0)/dn \ , \tag{11a}$$

$$\beta=4\pi n_0 \ . \tag{11b}$$

From Eqs. (10a) and (10b) it is seen that, for large x inside the metal, both $\phi(x)-\mu$ and $Q(x)$ behave as e^{kx}, with k given by

$$(\lambda/4)k^4-\alpha k^2+\beta=0 \ . \tag{12}$$

Table I shows the values of the real and imaginary part of k for the alkali metals; it is seen that it is a complex number in all cases; this means that the electronic density $n(x)$ oscillates,

$$n(x)=n_0[1+Ae^{k_r x}\cos(k_i x+\delta)] \ . \tag{13}$$

These oscillations are similar in structure to the Friedel oscillations found in the self-consistent solution of Lang and Kohn. This is a largely unknown fact for the Thomas-Fermi-von Weizsäcker (TFW) function. One must point out, however, that these oscillations are not Friedel oscillations, since their wave number is not $2k_f$ and their decay is exponential. The constants A and δ cannot be determined from the present, linear analysis. It is also interesting to observe that the constant k is also complex even in the absence of exchange and correlation, $\epsilon_{\mathrm{xc}}=0$, as shown in Table II. This is an unexpected result, since one would expect that the oscillations would be driven precisely by the exchange-correlation interaction; the only possible explanation is that they are driven by the gradient correction. Note also that the exact solution of the semi-infinite surface problem satisfies the Budd-Vannimenus[6] theorem, a fact that could be used in a numerical approach as a test on self-consistency.

TABLE I. Values of the decay constants for several simple metals, as a function of the density parameter r_s. Values were obtained for $\lambda=\frac{1}{9}$, and Wigner exchange-correlation energy.

Metal	r_s (a.u.)	$2k_f$ (a.u.)	k_r (a.u.)	k_i (a.u.)
Li	3.28	1.170	1.146	0.661
Na	3.99	0.962	0.924	0.671
K	4.96	0.774	0.716	0.740
Rb	5.23	0.734	0.671	0.767
Cs	5.63	0.682	0.611	0.806

II. NUMERICAL APPROACH

At first glance it may seem that solving the system under study would hardly pose any difficulty. This, however, is not the case, since the system of equations is not stable. The nature of this instability is mainly electrostatic, since it is only for the correct solution that one satisfies the charge neutrality requirement. Aside from this very important point, it is common knowledge that the system is most easily solved if one uses the dependent variable $u(x)$ previously defined, instead of $n(x)$, since the system becomes somehow less unstable.

To solve our system, it is preferable to write it as a system of first-order differential equations; in this way one can use a Runge-Kutta integration method. The system is

$$\frac{du}{dx}=v \ , \tag{14a}$$

$$\frac{dv}{dx}=(2/\lambda)[1/2(3\pi^2 n)^{2/3}+V_{\mathrm{xc}}+\phi-\mu]u \ , \tag{14b}$$

$$\frac{d\phi}{dx}=w \ , \tag{14c}$$

$$\frac{dw}{dx}=4\pi[n_+(x)-n(x)] \ . \tag{14d}$$

Consider now the boundary conditions that must be imposed upon the solution. Let us consider the case of a jellium slab of width $2L$, with ionic density profile

$$n_+(x)=\begin{cases} n_0 & \text{if } x\in(-L,L), \\ 0 & \text{otherwise} \ . \end{cases} \tag{15}$$

Observe that the value of the chemical potential μ can be chosen as zero; if the integration is started from a point $x=R$ (in the asymptotic region) inwards, then

$$u(R)=n_0^{1/2}e^{-\omega(x-x_0)/2} \ , \tag{16a}$$

$$v(R)=-\omega u(R) \ , \tag{16b}$$

$$\phi(R)=\phi(\infty)-\pi[u(R)/\omega]^2 \ , \tag{16c}$$

$$w(R)=2\pi u^2(R)/\omega \ . \tag{16d}$$

Note that ω and $\phi(\infty)$ are related by Eq. (9), with the choice $\mu=0$. From the symmetry of the slab one has

$$\frac{du(x=0)}{dx}=0 \ , \tag{17a}$$

TABLE II. Decay parameters of jellium, for $\epsilon_{\mathrm{xc}}(n)=0$. The values of the decay constants for Al and Pb are real, therefore the two real solutions are given

Metal	r_s (a.u.)	$2k_f$ (a.u.)	k_r (a.u.)	k_i (a.u.)
Al	2.07	1.854	2.367	0.666
Pb	2.30	1.669	2.251	0.944
Zn	2.65	1.448	1.810	0.361
Li	3.28	1.170	1.769	0.989
Na	3.99	0.962	1.365	0.955
K	4.96	0.774	0.959	0.146
Rb	5.23	0.734	0.916	0.175
Cs	5.63	0.682	0.859	0.201

TABLE III. Work functions for the alkali metals.

Metal	r_s (a.u.)	Φ Present[a] (eV)	Present[b] (eV)	Ref. 4 (eV)	Ref. 3 (eV)
Li	3.28	3.32	2.87	3.11	3.37
Na	4.00	2.60	2.59	2.93	3.06
K	4.96	2.38	2.29	2.76	2.74
Rb	5.23	2.33	2.22	2.71	2.63
Cs	5.63	2.25		2.64	2.49

[a] Jellium model.
[b] Pseudojellium model.

$$\frac{d\phi(x=0)}{dx}=0 . \tag{17b}$$

Condition (17b) is equivalent to charge neutrality. Given ω and x_0, a solution is uniquely determined. To find the proper solution one must satisfy Eqs. (17), which constitute a system of nonlinear equations. Define

$$F(\omega,x_0)=\frac{du(x=0)}{dx} , \tag{18}$$

$$G(\omega,x_0)=\frac{d\phi(x=0)}{dx} . \tag{19}$$

To obtain the solution that we seek, we must find the roots of (18) and (19). This is done by Newton's method, which converges rapidly once a reasonable starting point is found. Observe that one must make sure that a true minimum of the functional has been found. Normally, it is enough to require that the function $u(x)$ has no nodes.

III. RESULTS

The method described above has been applied to study the electronic properties of alkali-metal slabs, in particular, the work function and surface energy as a function of slab width. The results obtained can be described as follows: Concerning the work function it is found that, for the metals studied, it approaches its bulk value very rapidly; for example, a slab of sodium of size 5.0 a.u. already has a work function that corresponds to the semi-infinite surface. The calculated values for the work function are presented in Table III, third column. A comparison with the work functions obtained by Smith and the present work shows that they are quite close, within 0.2 eV, and within 0.5 eV of Lang and Kohn's.

For the surface energy the situation is more complex. To describe it properly, the surface energy can be split into its Thomas-Fermi (TF), gradient (gr), electrostatic (es), and exchange-correlation components (xc). If one looks at the total surface energy as a function of the slab width, it is observed that up to a length of up to 10 a.u. it has not yet converged to its bulk value (it oscillates). The bulk of the contribution to this variation comes from the Thomas-Fermi and the exchange-correlation parts, which are always larger than the gradient and electrostatic parts. The reason of this oscillation can be understood as follows: The density at the center of the slab, $n(L)$, is an oscillatory function of L, and it correlates very well with the (surface) energy oscillations; these oscillations will persist as long as $n(L)$ has not settled to n_0. This situation reminds one of similar oscillations in the case of small metallic particles.[7] The oscillations in surface energy represent a variation of the order of 10% of the total, so it may be said that the surface energy will remain within these bounds. With this proviso one can take the values given in Table IV as the surface energy of a metal in the TFW approximation.

To compare with Warner's results, a calculation was made for a cesium slab of width 5.1 a.u. The difference between the two solutions is impossible to notice visually, in spite of the fact that the solutions satisfy different boundary conditions. The boundary condition used by Warner was to require the density to vanish at a large (but finite) distance from the metal surface. The present solution, instead, has the correct asymptotic behavior far from the slab. This difference could account for the slight difference between Warner's work function, $W=2.24$ eV, and the present, $W=2.25$ eV. Surface energies were not reported in Warner's work; here $\sigma=48$ erg/cm^2, to be compared with Lang and Kohn's $\sigma=70$ erg/cm^2.

In a recent article,[8] a model has been introduced to calculate the electronic properties of inhomogeneous metallic systems. It was found that this model, the pseudojellium model, is able to describe very accurately the surface energy of simple metals. The procedure here is to modify the

TABLE IV. Components of the surface energy for the alkali metals (jellium model; energies in erg/cm^2).

Metal	σ_{TF}	σ_{gr}	σ_{es}	σ_{xc}	σ	Ref. 4	Ref. 3
Li	−396	94	45	369	112	132	210
Na	−150	53	12	187	101	111	160
K	−41	28	3	68	59	69	100
Rb	−26	24	3	47	48		85
Cs	−22	20	2	48	48		70

TABLE V. Surface energies in the pseudojellium model, as calculated with the TFW approach.

Metal	$\sigma_{\rm TF}$	$\sigma_{\rm gr}$	$\sigma_{\rm es}$	$\sigma_{\rm xc}$	$\sigma_{\Delta\rm xc}$	σ
Li	−411	107	30	420	55	200
Na	−142	52	12	171	−3	90
K	−61	25	5	104	−13	90
Rb	−44	21	3	80	−11	50

exchange-correlation energy by the addition of an extra term, $\Delta\varepsilon_{\rm xc}(n)$, inside of the metal, which amounts to modifying the chemical potential of the jellium to obtain that of the real metal, by adding a correction $\Delta\mu$.[8] With this, the calculated surface energy can be directly compared with experimental data. This was done in Ref. 8 by solving the Kohn-Sham equations, with good results. Here the same procedure is applied, except that the electronic density is directly computed from the solution of the Euler equation (6). The fourth column of Table III shows the results obtained for the work function, again in good order of magnitude agreement with the results of Lang and Kohn. Note, however, that pseudojellium work functions have a tendency to be smaller than their jellium counterparts. This is contrary to what happens when one does a full Lang-Kohn calculation with pseudojellium correction, as it was done in Ref. 8. The reason for this is not clear presently. The surface energy was also studied, with the results shown in Table V. To present the results, the surface energy σ was split as before, but with an additional Δxc component. The behavior as a function of slab size was found to be the same as that the pure jellium case. The surface energies are again in reasonable agreement with experiment.

The shape of the solution for the electronic density $n(x)$ is not very different from the Thomas-Fermi solution, since the oscillations that, according to Eq. (13) should be present, are not seen. This could be attributed to the fact that the equations have been solved only for a slab, and not for the semi-infinite surface. However, it seems more likely that the oscillations are of very small amplitude, since they must decay exponentially. In conclusion, the test of the TFW approach that is reported here shows that one can obtain good estimates of the electronic properties of metallic surfaces. The major difficulty here seems to lie in the fact that the equations to be solved are unstable. A solution for this may already have been found. In a recent article, Levy, Perdew, and Sahni[9] proposed an exact equation to treat any system with an explicitly known kinetic-energy functional, such as those proposed by Ma and Sahni.[10] It remains to be seen if the instability problem is avoided with that procedure.

ACKNOWLEDGMENTS

The author wishes to acknowledge Professor Herbert B. Shore, Professor Viraht Sahni, and Professor John Perdew for their invaluable comments. This work was supported in part by Fondo Nacional de Desarrollo Científico y Tecnológico (FONDECYT) Grant No. 5078 and Departamento de Investigatión y Bibliotecas (DIB), Universidad de Chile, Grant No. E-2286-8623.

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