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Exact solution of metal surface properties in square barrier and linear one-electron potential models

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The exact solution is given for the electron density and various electrostatic properties of the infinite- and finite-square-barrier model for the effective potential of a jellium metal surface. It is shown that the analytic results usually given for the electrostatic potential at the surface, the surface dipole barrier and the work function of these models, do *not* correspond to the exact solution. We find those quantities to depend sensitively on the electron density outside the surface region. The electrostatic part of the surface energy however, is found to be insensitive to the precise form of the electron density outside the surface region. These observations also apply to the linear-potential model for the effective one-electron potential.

I. INTRODUCTION

Currently there is great interest in simple models for the effective one-electron potential[1] near a metal surface, for which an analytic expression for the electron density can be obtained. Fully self-consistent solutions for the electron density are numerically cumbersome, so that even the solution of this problem for the jellium model of a metal surface has been a great achievement.[2-4] Moreover, such solutions give the electron density only numerically. It is therefore a great advantage if models can be found that permit an analytic solution for the electron density that closely approximates the result of a fully-self-consistent calculation of the density for the same system. The evaluation of various surface properties is greatly facilitated and the results can be expected to approach those of a self-consistent calculation closely since the densities in both cases are similar.[5] In addition, the availability of analytic densities can be very helpful for the study of fundamental questions concerning the inhomogeneous electron gas, such as the feasibility of gradient expansions[6] or the merits of the local-density approximation for the exchange and correlation energy.[7]

Unfortunately, there are not many model potentials for which the electron density can be obtained analytically. And for those it remains to be seen whether they give rise to an acceptable density profile i.e., one close to the self-consistent result for the system under consideration. However, for the jellium model of a metal surface, both good results for the self-consistent density[2,3] and for effective one-electron model potentials are available. Of the latter, the infinite and finite-square-barrier potentials have been known for a long time.[8-10] They have been considered recently merely as a device to generate electron densities close to the self-consistent result,[7] but also more directly as approximations to the self-consistent effective one-electron potential itself.[11,12] Recently, linear potentials whose densites approximate self-consistent densities more closely have been studied extensively[13,14]; these also give better results for various metal surface properties.

The purpose of the present paper is to show that, contrary to the general understanding in the square-barrier or linear-potential models, the familiar analytic results for the electrostatic potential, dipole barrier, and work function do *not* correspond to the exact solution for these quantities. The exact solution will be given and its relation to the familiar results elucidated. We want to stress immediately that our results do not invalidate some of the work mentioned above; in fact, the usual method of generating electron densities may be an even better prescription than that imposed by the exact solution. We wish to point out however that the *exact* solution gives rise to different results from those usually assumed to be the case. In view of the wide interest in these models, we feel that this is an important observation.

The paper is set out as follows: in Sec. II, the model is explained, and the expressions for the potential, electron density, and surface dipole presented. In Sec. III, the explicit forms for these quantities are given for the infinite-square-barrier model. In Sec. IV, the finite-square-barrier model is discussed, and Sec. V has the conclusions.

II. MODEL

In order to establish our notation, we first define the well-known square-barrier models.[4,9,10]

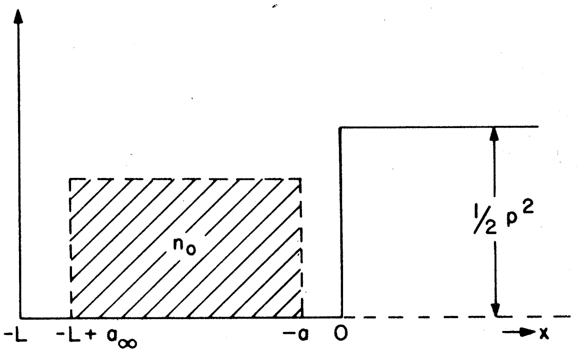

FIG. 1. Configuration of the square-barrier model.

Let us consider a rectangular metal sample of volume $V = L_x L_y L_z$, in which the ions are replaced by a uniform charge distribution of density n_0. At the (010) and (001) faces of the sample one imposes periodic boundary conditions on the wave function of a conduction electron. Each electron moves independently in an effective one-electron potential along the x direction of square barrier type with a step of height $W = p^2/2$ at $x = 0$. The (100) surface of interest is located at $x = -a$, at the other (100) face one imposes hard-wall boundary conditions on the electron wave functions. That is to say, there is an infinite barrier at $x = -L \equiv -(L_x + a + a_\infty)$ with the surface at $x = -L + a_\infty$ (see Fig. 1). Both a and a_∞ are determined by the requirement of charge neutrality. We refer to the end of Sec. IV for a discussion of the independence of the surfaces at $x = -a$ and $x = -L + a_\infty$. It is a matter of taste to define the geometry and boundary conditions in this way. The results obtained below apply equally well to one surface of a metal slab centered at $x = 0$ with step boundaries at both (100) faces.[10]

The one-electron wave functions are given by

$$\Psi_{\vec{k}}(\vec{r}) = \frac{1}{(L_y L_z)^{1/2}} e^{i\vec{k}_\parallel \cdot \vec{r}_\parallel} \varphi_k(x), \quad \vec{k}_\parallel = (k_y, k_z) \tag{2.1}$$

and

$$\varphi_k(x) = -\left(\frac{2\gamma}{\gamma L + 1}\right)^{1/2} \sin\delta\, e^{-\gamma x}, \quad x \geq 0, \tag{2.2a}$$

$$\varphi_k(x) = \left(\frac{2\gamma}{\gamma L + 1}\right)^{1/2} \sin(kx - \delta), \quad -L \leq x \leq 0, \tag{2.2b}$$

and

$$\gamma = (p^2 - k^2)^{1/2}; \quad \delta = \arcsin(k/p). \tag{2.3}$$

The possible values of k are

$$kL = n\pi - \delta, \quad n = 1, 2, 3, \ldots . \tag{2.4}$$

This result follows straightforwardly from the Schrödinger equation

$$(-\nabla^2 + p^2)\varphi_k(x) = k^2 \varphi_k(x), \quad x \geq 0,$$

$$-\nabla^2 \varphi_k(x) = k^2 \varphi_k(x), \quad -L \leq x \leq 0$$

and the appropriate boundary conditions at $x = -L$ and $x = 0$. Atomic units are adopted throughout $(m_e = \hbar = |e| = 1)$. If one recalls that the number of allowed values for $\vec{k}_\parallel$ at fixed k is $(1/4\pi) L_y L_z (k_F^2 - k^2)$, and takes the spin degeneracy into account the electron number density $n_e(\vec{r})$ for the ground state is found to be

$$n_e(\vec{r}) = 2 \sum_{\vec{n}} |\Psi_{\vec{k}}(\vec{r})|^2 = \frac{1}{2\pi} \sum_{n=1}^{N} (k_F^2 - k^2) |\varphi_k(x)|^2,$$

where N is the integer belonging to the Fermi-level electron. Or, on substitution of (2.2),

$$n_e(x) = \frac{1}{\pi} \sum_{n=1}^{N} (k_F^2 - k^2) \sin^2\delta\, e^{-2\gamma x} \left(\frac{\gamma}{\gamma L + 1}\right), \quad x \geq 0 \tag{2.5a}$$

$$n_e(x) = \frac{1}{\pi} \sum_{n=1}^{N} (k_F^2 - k^2) \sin^2(kx - \delta) \left(\frac{\gamma}{\gamma L + 1}\right), \quad -L \leq x \leq 0 \tag{2.5b}$$

From Poisson's equation one has for the electrostatic potential $\varphi(x)$, defined to be zero as $x \to -\infty$, (by which is meant a point deep in the interior of the metal)

$$\varphi(x) = -4\pi \int_x^\infty dx' \int_{x'}^\infty dx'' n_T(x'') + \Delta\varphi \equiv \psi(x) + \Delta\varphi, \tag{2.6}$$

with

$$\Delta\varphi = \varphi(\infty) - \varphi(-\infty) = 4\pi \int_{-\infty}^{+\infty} dx' \int_{x'}^{+\infty} dx'' n_T(x''). \tag{2.7}$$

Here

$$\begin{aligned} n_T(x) &= n_e(x) - n_{\text{background}} \\ &= n_e(x) - n_0 \Theta(-x - a) \Theta(x + L - a_\infty). \end{aligned} \tag{2.8}$$

$\Delta\varphi$ is also conveniently expressed as

$$\Delta\varphi = 4\pi \int_{-\infty}^{+\infty} dx\, x n_T(x). \tag{2.9}$$

Writing the electronic and background part separately $[\psi(x) = \psi_e(x) + \psi_B(x)]$ and using (2.5), (2.6), and (2.8), one readily finds

$$\psi_e(x) = \sum_{n=1}^{N} (k_F^2 - k^2) \frac{\gamma}{\gamma L + 1}\left(-x^2 + \frac{\sin 2\delta}{k} x + \frac{\cos 2\delta}{2k^2} - \frac{\cos[2(kx-\delta)]}{2k^2}\right) + \frac{2x}{p^2} \sum_{n=1}^{N} \frac{(k_F^2 - k^2)k^2}{(\gamma L + 1)}$$
$$- \frac{1}{p^2} \sum_{n=1}^{N} (k_F^2 - k^2) \frac{k^2}{\gamma(\gamma L + 1)}, \quad -L \leqslant x \leqslant 0, \qquad (2.10a)$$

$$\psi_e(x) = - \frac{1}{p^2} \sum_{n=1}^{N} (k_F^2 - k^2) k^2 \frac{e^{-2\gamma x}}{\gamma(\gamma L + 1)}, \quad x \geqslant 0, \qquad (2.10b)$$

and

$$\psi_B(x) = -2\pi n_0 (L - a_\infty)^2 - 4\pi n_0 (L - a - a_\infty)x + 2\pi n_0 a^2, \quad -L \leqslant x \leqslant -L + a_\infty, \qquad (2.11a)$$

$$\psi_B(x) = 2\pi n_0 (x + a)^2, \quad -L + a_\infty \leqslant x \leqslant -a, \qquad (2.11b)$$

$$\psi_B(x) = 0, \quad x \geqslant -a. \qquad (2.11c)$$

All of the above expressions are well known, but, to our knowledge, it has escaped attention that the usual analytic results for the electrostatic dipole barrier and work function of these models do *not* correspond to the exact solution.

The magnitude of the electrostatic surface dipole barrier depends, of course, on the way this quantity is defined.[8] It is usually defined as[4]

$$\langle \Delta\varphi \rangle = \varphi(\infty) - \overline{\varphi}, \qquad (2.12)$$

where $\overline{\varphi}$ is the average of the electrostatic potential over the metal sample:

$$\overline{\varphi} = \frac{1}{V} \int_{\text{metal}} d\vec{r}\, \varphi(\vec{r}). \qquad (2.13)$$

In another definition, the dipole barrier is measured with respect to some specific point in the interior of the metal. An example is the expression given by (2.7),

$$\Delta\varphi = \varphi(\infty) - \varphi(-\infty) = 4\pi \int_{-\infty}^{+\infty} dx' \int_{x'}^{+\infty} dx''\, n_T(x''). \qquad (2.7)$$

It may often happen (see Ref. 4, page 247) that $\overline{\varphi} \approx \varphi(x_\infty)$ for any point x_∞ chosen in the metal interior well outside the surface region. In that case (2.12) and (2.7) lead to the same result for the electrostatic dipole barrier. However, for the infinite- and finite-square-barrier models this is not the case. It turns out that $\overline{\varphi} \neq \varphi(-\infty)$. Remember that $\varphi(-\infty)$ is defined to be zero, because of the choice of boundary conditions in (2.6). Moreover, the exact results for $\Delta\varphi$ (and by the same token for the work function) differ from the expressions presently adopted, e.g., for the infinite square barrier model it turns out that $\Delta\varphi$ equals $(k_F/\pi)(1 - \frac{3}{32}\pi^2 + \frac{1}{24}\pi^2)$, *not* $(k_F/\pi)(1 - \frac{3}{32}\pi^2)$. We present the derivation of these results in Sec. III.

III. INFINITE-SQUARE-BARRIER MODEL

We shall first treat the infinite square barrier model, since in this case the *exact* expressions for the electrostatic dipole barrier and work function can be obtained without making extensive use of the Euler-Maclaurin expansion, as is necessary for the finite barrier model.

A. Exact density

Letting $p \to \infty$ in (2.5) one obtains for the electron density

$$n_e(x) = 0, \quad x \geqslant 0,$$
$$n_e(x) = \frac{1}{2\pi L} \sum_{n=1}^{N} (k_F^2 - k^2) - \frac{1}{2\pi L} \sum_{n=1}^{N} (k_F^2 - k^2) \cos 2kx, \quad -L \leqslant x \leqslant 0, \qquad (3.1)$$

with $k = n\pi L$.

The sums in (3.1) can be readily evaluated and one finds

$$n_e(x) = n_0 - \frac{k_F}{12L^2} + \frac{k_F}{4L^2} \frac{\cos(2k_F x)}{\sin^2(\pi x/L)} - \frac{\pi}{8L^3} \frac{\sin(2k_F x)\cot(\pi x/L)}{\sin^2(\pi x/L)}$$
$$\equiv n_0 + \rho(x). \qquad (3.2)$$

The total density, therefore, is

$$n_T(x) = \rho(x), \quad -L + a_\infty \leqslant x \leqslant -a_\infty,$$
$$n_T(x) = n_0 + \rho(x), \quad -L \leqslant x \leqslant -L + a_\infty \text{ or } -a_\infty \leqslant x \leqslant 0. \qquad (3.3)$$

In the limiting case $|x|/L \ll 1$, valid near the metal surface, one obtains the result usually given for the electron density

$$n_e(x) \approx n_0[1 + (3/y^3)(y \cos y - \sin y)] \quad (y = 2k_F x). \qquad (3.4)$$

Since one is interested in surface properties, it is natural to use (3.4). We shall see, however, that for these models not all surface quantities depend solely on the electron density in the surface region. As a consequence, if one uses (3.4), one actually obtains the surface properties of a model in which the density near the surface is generated by a square barrier model and the resulting expression is subsequently assumed to hold throughout the entire sample. As we stated earlier, this procedure may be just as valuable for the purpose of generating a desirable electron density as any other; however, it does not correspond to the exact solution of the square barrier model.

B. Charge-neutrality condition

The charge neutrality condition, which fixes a_∞,[8-10] reads

$$\int_{-L}^{\infty} n_T(x)\,dx = 0,$$

or, for the infinite-barrier model,

$$\int_{-L}^{0} \rho(x)\,dx + \int_{-L}^{-L+a_\infty} n_0\,dx + \int_{-a_\infty}^{0} n_0\,dx = 0.$$

The first integral can be evaluated straightforwardly[15] [using GR(2.539.1)] and one finds

$$-k_F/12L - k_F^2/4\pi + 2a_\infty k_F^3/3\pi^2 = 0$$

or

$$a_\infty = 3\pi/8k_F + \pi^2/8k_F^2 L. \tag{3.5}$$

Apart from the familiar term of order unity,[10] there is a term of order L^{-1} that should be kept, since it will give contributions of order unity later on.

C. Electrostatic surface dipole barrier

In this section the dipole barrier is defined to be $\Delta\varphi = \varphi(0) - \varphi(-\frac{1}{2}L)$. The electrostatic potential $\psi(x)$, defined by (2.6), and given by (2.10) and (2.11), reduces ($p \to \infty$) to

$$\psi_e(x) = \frac{-x^2}{L} \sum_n (k_F^2 - k^2) + \frac{1}{2L} \sum_n \frac{k_F^2 - k^2}{k^2} \cos(2kx) + \frac{1}{2L} \sum_n \frac{k_p^2 - k^2}{k^2}, \tag{3.6}$$

$$\begin{aligned} \psi_B(x) &= -2\pi n_0 (L - a_\infty)^2 - 4\pi n_0 (L - 2a_\infty)x \\ &\quad + 2\pi n_0 a_\infty^2, \quad -L \leqslant x \leqslant -L + a_\infty, \\ \psi_B(x) &= 2\pi n_0 (x + a_\infty)^2, \quad -L + a_\infty \leqslant x \leqslant -a_\infty, \\ \psi_B(x) &= 0, \quad x \geqslant -a_\infty. \end{aligned} \tag{3.7}$$

$\Delta\varphi$ can be evaluated either by means of (2.9), $= 4\pi \int_{-L/2}^{0} dx\, x n_T(x)$, or by calculating $\psi(0)$ and $\psi(-\frac{1}{2}L)$ directly from (3.6) and (3.7). In the first approach the integrals, resulting after substitution of the exact density (3.2), can be done analytically [GR(2.539.3)], neglecting contributions of order $1/L$ and higher in the final result. The cases N = even and N = odd have to be distinguished, but the final result is the same whether N is even or odd.

The alternative approach is explicitly given in an Appendix, since it exemplifies the features of all calculations e.g., the fact that the term of order L^{-1} in a_∞ should be kept. Here we only state the result:

$$\psi(-\tfrac{1}{2}L) = -\frac{k_F}{\pi} + \frac{3\pi k_F}{32} - \frac{\pi k_F}{24} \quad \text{and} \quad \psi(0) = 0.$$

Hence

$$\Delta\varphi = \frac{k_F}{\pi}\left(1 - \frac{3\pi^2}{32} + \frac{\pi^2}{24}\right) \tag{3.8}$$

and not $(k_F/\pi)(1 - 3\pi^2/32)$, as would be the case if (3.4) held throughout the sample.

D. Average electrostatic potential

The average of the electrostatic potential over the metal sample ($\overline{\varphi}_{L_x}$) can be obtained from (3.6) and (3.7). First the x integrations are performed. The algebra for evaluation of various sums is entirely similar to the calculation given as an example in the appendix. Again, the term of order L^{-1} in a_∞ is of crucial importance. Instead of taking the average over the metal, one may take the average over the potential well ($\overline{\varphi}_L$). It turns out that $\overline{\varphi}_{L_x} = \overline{\varphi}_L$, which explicitly bears out a remark made in Ref. 4 (page 241, footnote 62). However, for the average itself, one finds

$$\overline{\varphi}_{L_x} = \overline{\varphi}_L = \frac{\pi k_F}{72} - \Delta\varphi$$

or in terms of $\varphi(x)$, defined to be zero at $x = -L/2$ by (2.6),

$$\overline{\varphi}_{L_x} = \overline{\varphi}_L = \overline{\varphi} = \frac{\pi k_F}{72} \tag{3.9}$$

instead of $\overline{\varphi} = 0$. Therefore, it does indeed not matter where precisely one takes the boundary of integration in the surface region,[4] but, at least for these models, the average electrostatic potential itself is *not* equal to its value at any specific point in the interior of the metal.

E. Electrostatic potential at the surface

In view of promising applications of a theorem due to Budd and Vannimenus[16] to the calculation of surface properties,[12,13] it is of interest to know the electrostatic potential at the surface, i.e., for $x = -a_\infty$. Since $x/L \ll 1$ in the surface region, the last term of (3.6) can be reduced as follows:

$$\begin{aligned}\frac{k_F^2}{L}\sum_{n=1}^{N}\frac{\cos(2kx)}{k^2} &= \frac{1}{L}\left(\frac{k_F L}{\pi}\right)^2\left[\sum_{n=1}^{\infty}\frac{\cos(2\pi xn/L)}{n^2}-\sum_{n=N+1}^{\infty}\frac{\cos(2\pi xn/L)}{n^2}\right]\\ &\simeq \frac{1}{L}\left(\frac{k_F L}{\pi}\right)^2\left[\frac{\pi^2}{6}-\frac{\pi}{2}\left(\frac{2\pi|x|}{L}\right)+\frac{1}{4}\left(\frac{2\pi|x|^2}{L}\right)-\int_N^{\infty}dn\,\frac{\cos[(2\pi x/L)n]}{n^2}\right]\\ &\simeq \frac{k_F^2 L}{6}-\frac{2k_F^2|x|}{\pi}\left(\frac{\cos(2k_F|x|)}{2k_F|x|}+\mathrm{Si}(2k_F|x|)\right).\end{aligned}$$

For $|x|=a_\infty$, (3.1) and (3.2) then yield

$$\varphi(-a_\infty)=-\frac{3\pi k_F}{16}+\frac{\pi k_F}{24}+\frac{2k_F}{3\pi^2}\sin\frac{3\pi}{4}+\frac{k_F}{2\pi}\cos\frac{3\pi}{4}+\frac{3k_F}{8}\mathrm{Si}\left(\frac{3\pi}{4}\right). \tag{3.10}$$

Again, this result differs by $\pi k_F/24$ from the corresponding expression that is obtained if the expression for the electron density near the surface is extended to be valid over the whole sample.[11]

In addition, a point has to be made about the use of the Budd-Vannimenus theorem for square-barrier models. For reasons of clarity we state the results of Ref. 16(b), where it is shown, that the change (ΔE) in total energy of N electrons in the groundstate, upon stretching a jellium slab uniformly (which produces a change Δn_0 of the uniform background density), is given in terms of the electrostatic potential $\varphi(x)$ by

$$\frac{1}{V}\frac{\Delta E}{\Delta n_0}=\varphi(-a_\infty)-\varphi_0+\frac{2}{L_x}\int_{-L/2}^{-a_\infty}[\varphi_0-\varphi(x)]dx. \tag{3.11}$$

This is expression (4) of Ref. 16(b), displayed for the infinite-barrier model in our notation.[16(c)] Budd and Vannimenus show that this result is independent of the choice of $G[n]$, the universal functional describing the contribution of kinetic energy, exchange, and correlations to the total ground-state energy. In the limit of large L_x the total energy can be split in a bulk and a surface part: $E(n_0) = Nf(n_0)+2L_yL_z\sigma(n_0)$, where $f(n_0)$ and $\sigma(n_0)$ are the bulk and surface energy per particle, respectively. Hence [expression (5) of Ref. 16(b)]

$$\frac{1}{V}\frac{\Delta E}{\Delta n_0}=n_0\frac{df}{dn_0}+\frac{2}{L_x}\frac{d\sigma}{dn_0}. \tag{3.12}$$

Or, by comparison of the leading terms in (3.11) and (3.12),

$$n_0\frac{df}{dn_0}=\varphi(-a_\infty)-\varphi_0. \tag{3.13a}$$

And, under the assumption (clearly stated by Budd and Vannimenus) that $\varphi(-a_\infty)-\varphi_0$ tends to its asymptotic value faster than L_x^{-1} one also finds

$$\frac{d\sigma}{dn_0}=\lim_{L_x\to\infty}\int_{-L/2}^{-a_\infty}[\varphi_0-\varphi(x)dx]. \tag{3.13b}$$

Now, for the finite- and infinite-square-barrier models, the usual procedure is to obtain the electron density for the ground state from the wave functions of the model potential. Once this density has been calculated, the total ground-state energy may be obtained in principle.[5] Here, the kinetic energy can be calculated directly,[9,10] the electrostatic energy follows from Poisson's equation and for exchange and correlations approximations can be made[11-14] without affecting the validity of the BV theorem since it is independent of the choice of $G[n]$. In addition, however, in order that both (3.13a) and (3.13b) hold for the barrier models, $\varphi(-a_\infty)-\varphi_0$ has to tend to its asymptotic value faster than L_x^{-1}. This can be tested explicitly for the infinite square barrier (the case we have concentrated on for definiteness throughout this section) as well as for the finite-barrier model. For the infinite-barrier model, then, the right-hand side of (3.11) can be calculated explicitly to order L_x^{-2} using (3.6) and (3.7). We find that $[\varphi_0-\varphi(-a_\infty)]$ does *not* tend to its asymptotic value faster than L_x^{-1}; therefore, the identification made by Budd and Vannimenus [Eq. (3.13b)] is not correct for the present case. In fact, $\varphi(-a_\infty)-\varphi_0$ contains L_x^{-1} terms, coming from both terms, which would have to be added to the right-hand side of (3.13b) in order to identify the surface terms. Expression (3.13a), being (3.11) to order unity, still holds, but for φ_0 one has to read the average electrostatic potential $\bar{\varphi}$ since it differs by a term of order unity ($k_F\pi/72$) from its value at the center. This again shows that one has to be careful to distinguish between the average electrostatic potential and its value deep inside the sample.

F. Electrostatic part of the surface energy

The electrostatic part of the surface energy (σ_{es}) is given in terms of the electrostatic potential by

$$\sigma_{\mathrm{es}}=\frac{1}{8\pi}\int_{-L/2}^{0}\left(\frac{d\varphi}{dx}\right)^2dx. \tag{3.14}$$

Let us briefly indicate how this quantity is calculated. With the electrostatic potential given by (3.6) and (3.7) the integrand of (3.14) turns out to be

$$\begin{aligned}\left(\frac{d\varphi}{dx}\right)^2 &= \left[4\pi n_0 x\left(1-\frac{2a_\infty}{L}\right)\right]^2 - \frac{8\pi n_0 x}{L}\left(1-\frac{2a_\infty}{L}\right)\sum_{n=1}^{N}\frac{k_F^2-k^2}{k}\sin(2kx)\\ &\quad+\frac{1}{L^2}\sum_{n=1}^{N}\sum_{m=1}^{N}\left(\frac{k_F^2-k^2}{k}\right)\left(\frac{k_F^2-q^2}{q}\right)\sin(2kx)\sin(2qx),\quad kL=n\pi,\quad qL=m\pi,\quad 0\geqslant x\geqslant -a_\infty.\\ \left(\frac{d\varphi}{dx}\right)^2 &= \left[4\pi n_0 a_\infty\left(1+\frac{2x}{L}\right)\right]^2 + \frac{8\pi n_0 a_\infty}{L}\left(1+\frac{2x}{L}\right)\sum_{n=1}^{N}\frac{k_F^2-k^2}{k}\sin(2kx)\\ &\quad+\frac{1}{L^2}\sum_{n=1}^{N}\sum_{m=1}^{N}\left(\frac{k_F^2-k^2}{k}\right)\left(\frac{k_F^2-q^2}{q}\right)\sin(2kx)\sin(2qx),\quad -L+a_+\geqslant x\geqslant -a_+.\end{aligned}\tag{3.15}$$

Sums over possible k values that are encountered in the course of the calculation are ($a\equiv 3\pi/8k_F$, $b\equiv 3\pi/4$)

$$\sum_{n=1}^{N}\cos\left(\frac{2\pi a}{L}n\right)\approx\frac{L}{2\pi a}\sin(b),$$

$$\sum_{n=1}^{N}\frac{\cos[(2\pi a/L)n]}{n^2}\approx\frac{\pi^2}{6}-\frac{\pi\cos(b)}{k_F L}-\frac{2\pi a}{L}\,\mathrm{Si}(b),$$

$$\sum_{n=1}^{N}\frac{\sin[(2\pi a_\infty/L)n]}{n^3}\approx\frac{a_\infty\pi^3}{3L}-2\left(\frac{\pi a}{L}\right)^2\times\left[\frac{\cos(b)}{b}+\frac{\sin(b)}{b^2}+\mathrm{Si}(b)\right],$$

$$\sum_{n=1}^{N}\frac{(-1)^n}{n^2}\approx-\frac{\pi^2}{12},$$

and

$$\sum_{n=1}^{N}\left[k_F^2-\left(\frac{n\pi}{L}\right)^2\right]=\frac{2k_F^3L}{3\pi}-\frac{k_F^2}{2}-\frac{\pi k_F}{6L},$$

which has already been substituted into the above expression for $(d\varphi/dx)^2$. In every sum the terms are retained that give rise to contributions of (at least) order unity to σ_{es}. The various space integrals, resulting from (3.14) and (3.15), are performed, and for the sums k values the above expressions are substituted. After some straightforward but subtle algebra the following analytic expression for the electrostatic (part of the) surface energy is found:

$$8\pi\sigma_{es}=k_F^3\left[-\frac{2}{3\pi}-\frac{\pi}{16}+\frac{\sqrt{2}}{2}\left(\frac{1}{3\pi^2}-\frac{1}{4\pi}\right)+\mathrm{Si}(b)\left(\frac{3}{16}+\frac{2}{3\pi^2}\right)\right].\tag{3.16}$$

If the electrostatic surface energy is calculated from (3.14) and the density given by (3.4) *for all* x, the result obtained is identical to expression (3.16). In the above derivation of (3.14) various contributions of order L occur, which of course all cancel from the final result. Moreover, three terms of order unity from the L^{-1} term in (3.5) appear, namely, $\pi k_F^3/72$, $\pi k_F^3/36$, and $-\pi k_F^3/24$; however, they cancel in the final result (3.16). Therefore, the results for σ_{es} are identical for the electron density given by (3.2) and that given (for all x) by (3.4).[7] This indicates that, in this model, the surface energy is truly a surface quantity in the sense that it is determined by the electron density in the surface region alone, while the exact results for the surface dipole barrier and work function depend on the electron density beyond the surface region as well.

IV. FINITE-SQUARE-BARRIER MODEL

For a infinite square barrier, of height $p^2/2$ and characterized by the parameter $\beta=k_F/p$, (see Fig. 1) we find the difference between various familiar expressions and the exact results, obtained from the electron density given by (2.5), to be the same as for the infinite-square-barrier model. Let us first state the results, and then comment on their derivation. (i) The surface is fixed by charge neutrality at $x=-a$, where

$$a=a_\infty-D=3\pi/8k_F+\pi^2/8k_f^2L-D\tag{4.1}$$

and

$$D=\frac{3}{4k_F}\left[\frac{(1-\beta^2)^{1/2}}{\beta}+\frac{(2\beta^2-1)}{\beta^2}\arcsin(\beta)\right].\tag{4.2}$$

(ii) The electrostatic surface dipole barrier, defined to be

$$\Delta\varphi=\varphi(\infty)-\varphi(-L/2),$$

is given by

$$\Delta\varphi=\frac{k_F}{\pi}\left[2-\frac{2}{3}(k_Fa)^2-\frac{\pi\beta}{2}+\frac{\pi^2}{24}+\frac{\beta^2-1}{2\beta}\ln\left(\frac{1+\beta}{1-\beta}\right)\right],\tag{4.3}$$

which differs from the familiar expression[11] by $\pi k_F/24$. This is also true for the value of the electrostatic potential at the surface. (iii) The average electrostatic potential over the metal sample (or over the potential well) is given by

$$\overline{\varphi}=\pi k_F/72,\tag{4.4}$$

where $\varphi(-L/2)$ is again defined to be zero.

We restrict ourselves to general remarks about the way in which these results are arrived at, since the details are elaborate and not very instructive. The exact density for a finite barrier ($\beta \neq 0$), given by (2.5), cannot be evaluated as simply as for the infinite barrier ($\beta = 0$). For the latter case all sums can be evaluated exactly and result in expression (3.2) for the electron density. For $\beta \neq 0$, the sums in (2.5) have to be determined by means of an Euler-Maclaurin expansion.[17] If spatial integrals occur, it is always advantageous, however, to perform those first, and then evaluate each sum by an Euler-Maclaurin expansion. All higher terms in $1/L$ that contribute to the final results for dipole barrier, etc. at most to order $1/L$ are neglected. Note that this approach is quite different from that of the previous section, where we started out with the exact electron density. Therefore, taking the limit $\beta \to 0$ in the present calculation provides a useful check on whether all terms contributing to order unity have been accounted for.

The key element in the calculations turns out to be the fact that *second* order corrections in the Euler-Maclaurin expansion give contributions of order unity to electrostatic quantities. In a general notation we have[17]

$$\sum_{n=1}^{N} f(n) = \int_0^N f(x)\,dx - \tfrac{1}{2}f(0) + \tfrac{1}{2}f(N) + \frac{1}{12}\left(\frac{df}{dx}\bigg|_{x=N} - \frac{df}{dx}\bigg|_{x=0}\right) + \cdots,$$

where the dots stand for terms involving higher (odd) derivatives. It was recognized long ago[10] that the first-order correction $\frac{1}{2}[f(N) - f(0)]$ should be taken into account. We find that the second-order correction term should be taken along as well. For instance, the contribution of order L^{-1} in (4.1) is due to this term. As in the infinite-barrier model, it gives contributions of order unity to electrostatic quantities.

Finally, let us discuss the boundary at $x = -L$, that we chose to be a hard wall, and whose effect should be trivial no matter how one calculates the electrostatic properties of the finite barrier. Consider the dipole barrier to be calculated from (2.9), $\Delta\varphi_T = 4\pi \int_{-L}^{\infty} dx\, x n_T(x)$. The result is $\Delta\varphi_T = \Delta\varphi - \Delta\varphi_\infty$, with $\Delta\varphi$ given by (4.3) and $\Delta\varphi_\infty$ by (3.8). This is what one should expect since the integral is taken from $-L$ to infinity. But, in this approach, it is not *a priori* clear that the dipole barrier of the relevant surface (at $x = -a$) is given by $\Delta\varphi = \Delta\varphi_T + \Delta\varphi_\infty$. However, the value of the electrostatic potential at $x = -L$, $x = -L/2$, and $x = \infty$ can be evaluated directly from expressions (2.10) and (2.11); one finds $\varphi(\infty) - \varphi(-\frac{1}{2}L) = \Delta\varphi$ [given by (4.3)] and $\varphi(-\infty) - \varphi(-\frac{1}{2}L) = \Delta\varphi_\infty$ [given by (3.8)]. The latter result proves that $\varphi(-\infty) - \varphi(-\frac{1}{2}L)$ is independent of the height of the barrier at $x = 0$, so that indeed $\Delta\varphi = \Delta\varphi_T + \Delta\varphi_\infty$, if calculated by means of (2.9), is the dipole barrier of the finite barrier at $x = 0$, and the boundary at $x = -L$ is completely trivial, as it should be.

V. CONCLUDING REMARKS

We have not derived an analytic expression for the electrostatic part of the surface energy in the finite-barrier model. Considering the fact that the exact solution gives rise to the same additional contributions for the electrostatic potential in the infinite- and finite-barrier model, it is likely to leave the familiar result for the electrostatic surface energy[7] unchanged for the finite-barrier model, as it did for the infinite-barrier. Also we did not carry out a full analysis of the features discussed in this paper for the linear potential model.[12-14] It is, however, immediately clear that the same type of additional contributions, as discussed here, also occur for the exact solution of the linear model, since it transforms into the infinite-square-barrier model in the limit of the infinite slope. It may be that the additional terms depend upon the slope. However, in view of the fact that for finite-square-barrier models such terms are independent of the barrier height, we speculate that they will not depend upon the slope in the linear model either.

In order to give an impression of the changes that may be brought about by the additional contribution to the analytic solution, we follow an idea put forward in Ref. 11 to calculate the electrostatic surface dipole barrier. The barrier height is determined by the self-consistency requirement

$$1/2\beta^2 = (1/k_F^2)[\Delta\varphi(\beta) - \mu_{xc}(k_F)]. \tag{5.1}$$

Here $-\mu_{xc}(k_F)$ is the contribution to the barrier derived from the exchange and correlation energy in the uniform electron gas approximation. The expression for the dipole barrier now reads

$$\Delta\varphi(\beta) = \frac{k_F}{\pi}\left(2 - \frac{2}{3}(k_F a)^2 - \frac{\pi\beta}{2} + \frac{\beta^2 - 1}{2\beta} \ln \frac{1+\beta}{1-\beta} + \frac{\pi^2}{36}\right). \tag{5.2}$$

Here we chose to define $\Delta\varphi \equiv \varphi(\infty) - \overline{\varphi}$, and in that case $\pi k_F/36$ is the extra contribution due to analytic solution. Both β and $\Delta\varphi(\beta)$ can now be determined self-consistently from (5.1) and (5.2). The results are given in Table I, together with those of Ref. 11 and the self-consistent results of Lang and Kohn. The additional term in (5.2) gives rise to substantial changes. The agreement between $\Delta\varphi$ of (5.2) and the self-consistent results is better for high densities and even worse for

TABLE I. Self-consistently determined barrier height β and corresponding dipole barrier $\Delta\phi$ and work function Φ. For comparison the self-consistent results of Lang and Kohn are also given.

	Equation (5.2)			Reference 11			Lang-Kohn	
r_s	β	$\Delta\phi$	Φ	β	$\Delta\phi$	Φ	$\Delta\phi$	Φ
2.0	0.934	4.71	1.79	0.988	3.21	0.13	6.80	3.89
2.5	0.848	3.24	3.12	0.911	1.77	1.65	3.83	3.72
3.0	0.777	2.48	3.65	0.839	1.15	2.33	2.32	3.50
3.5	0.718	2.00	3.83	0.779	0.825	2.65	1.43	3.26
4.0	0.671	1.69	3.84	0.728	0.629	2.78	0.91	3.06
4.5	0.630	1.46	3.76	0.684	0.503	2.80	0.56	2.87
5.0	0.594	1.29	3.66	0.646	0.416	2.79	0.35	2.73
5.5	0.564	1.15	3.54	0.614	0.354	2.74	0.16	2.54
6.0	0.538	1.04	3.41	0.585	0.307	2.67	0.04	2.41

low densities than those of Ref. 11. We hasten to add, however, that we only want to display the difference between both models and that *neither* of the models results for $\Delta\varphi$ should be taken too seriously, because the densities of square-barrier models do not approximate the self-consistent densities very closely, and the magnitude of $\Delta\varphi$ is extremely sensitive to the discrepancies between those densities. For this reason the authors of Ref. 11 subsequently studied the linear potential model since it gives more promising density profiles. Moreover, by writing (5.1), the model potential is given the interpretation of a direct approximation to the self-consistent effective potential. In view of many conceptual subtleties,[18] it is not clear whether such a simple interpretation is permitted. Therefore, it makes more sense to consider the model potential merely as a means to generate acceptable analytic density profiles, and not to attach direct significance to the potential itself. Results for surface properties are then obtained, e.g., by fixing the parameter(s) in the potential through a variational calculation of the surface energy[7,14] or by application of the Budd-Vannimenus theorem.[12,13,16] Let us repeat once again that in the context of the latter approach the familiar analytic results may be just as good (or even preferable over) the exact results. This is an open question; we have shown in this paper that familiar results for the electrostatic potential and work function in square-barrier and linear-potential models differ from the exact results.

Finally, it should be mentioned that the use of exact electron density, say (3.2), instead of its approximation near the surface, (3.4), does not alter to order unity any expressions involving the kinetic-exchange or correlation-energy density. All corrections of this nature are found to be of higher order in $1/L$. Therefore, work in which these quantities are considered (e.g., Refs. 6, 7, and 19), is completely unaffected by the observations of this paper.

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APPENDIX

As an example of the algebra that can still be called palatable, we give the derivation of the surface dipole barrier for the infinite barrier model from expressions (3.6) and (3.7). From (3.6) we have

$$\psi_e(x) = -\frac{x^2}{L}\left(\frac{2k_F^3L}{3\pi} - \frac{1}{2}k_F^2 - \frac{\pi k_F}{6L}\right) + \frac{1}{2L}\left(\frac{k_F^2L^2}{6} - \frac{2k_FL}{\pi}\right) - \frac{1}{2L}\left[1 - \frac{1}{2}\sin(2k_Fx)\cot\left(\frac{\pi x}{L}\right) - \cos^2(k_Fx)\right] + F(x), \quad \text{(A1)}$$

with

$$F(x) = -\frac{k_F^2L}{2\pi^2}\sum_{n=1}^{N}\frac{\cos[(2\pi x/L)n]}{n^2}. \quad \text{(A2)}$$

In (A1) we have already performed the following sums up to the appropriate order in L^{-1} (which can be inferred from the coefficient in front of each sum):

$$\sum_{n=1}^{N}(k_F^2 - k^2) = k_F^2N - \left(\frac{\pi}{L}\right)^2\sum_{n=1}^{N}n^2 = \frac{k_F^3L}{\pi} - \frac{1}{6}\left(\frac{\pi}{L}\right)^3\left[2\left(\frac{k_FL}{\pi}\right)^3 + 3\left(\frac{k_FL}{\pi}\right)^2 + \frac{k_FL}{\pi}\right] = \frac{2k_F^3L}{3\pi} - \frac{1}{2}k_F^2 - \frac{\pi k_F}{6L} \quad \text{(A3)}$$

and

$$\sum_{n=1}^{N}\frac{k_F^2 - k^2}{k^2} = \left(\frac{k_FL}{\pi}\right)^2\sum_{n=1}^{N}\frac{1}{n^2} - N = \left(\frac{k_FL}{\pi}\right)^2\left(\sum_{n=1}^{\infty}\frac{1}{n^2} - \sum_{n=N+1}^{\infty}\frac{1}{n^2}\right) - N \approx \left(\frac{k_FL}{\pi}\right)^2\left(\frac{\pi^2}{6} - \int_N^{\infty}\frac{dn}{n^2} + \frac{1}{2N^2}\right) - N$$

$$= \frac{k_F^2L^2}{6} - \frac{2k_FL}{\pi} + \frac{1}{2} \approx \frac{1}{6}k_F^2L^2 - \frac{2k_FL}{\pi} + O(1). \quad \text{(A4)}$$

Furthermore, we have to the desired order

$$-\frac{1}{2L}\sum_{n=1}^{N}\cos\left(\frac{2\pi x}{L}n\right)$$
$$=-\frac{1}{2L}\left[1-\frac{1}{2}\sin(2k_F x)\cot\left(\frac{\pi x}{L}\right)-\cos^2(k_F x)\right]$$
$$\approx\frac{1}{4L}\sin(2k_F x)\cot\left(\frac{\pi x}{L}\right)+O(L^{-1}). \tag{A5}$$

For $F(x)$, defined by (A2), we find that the values of interest

$$F(0)=F(-L)=-k_F^2L/12+k_F/2\pi+O(L^{-1}) \tag{A6}$$

[the algebra for this case is already implicit in the derivation of (A4)] and

$$F(-\tfrac{1}{2}L)=k_FL/24+O(1). \tag{A7}$$

To arrive at the latter result we have to evaluate (take N even for definiteness)

$$-\frac{k_F^2L}{2\pi^2}\Bigg(\sum_{\substack{n=1\\ n\text{ odd}}}^{N}\frac{-1}{n^2}+\sum_{\substack{n=2\\ n\text{ even}}}^{N}\frac{1}{n^2}\Bigg)$$
$$=\frac{-k_F^2L}{2\pi^2}\Bigg(-2\sum_{\substack{n=1\\ n\text{ odd}}}^{N-1}\frac{1}{n^2}+\sum_{\substack{n=1\\ n\text{ all}}}^{N}\frac{1}{n^2}\Bigg)$$
$$\approx\frac{-k_F^2L}{2\pi^2}\left(-\frac{\pi^2}{4}+\frac{\pi^2}{6}+2\int_{N/2}^{\infty}dk\,\frac{1}{(2k+1)^2}-\int_{N}^{\infty}dk\,\frac{1}{k^2}\right)$$
$$=\frac{-k_F^2L}{2\pi^2}\left(-\frac{\pi^2}{12}+\frac{1}{N+1}-\frac{1}{N}\right)=\frac{k_F^2L}{24}+O(1).$$

Using the results (A3)–(A7) in expression (A1), we find

$$\psi_e(0)=0, \tag{A8a}$$
$$\psi_e(-L/2)=\frac{-k_F^3L^2}{6\pi}+\frac{k_F^2L}{4}+\frac{\pi k_F}{24}+\frac{k_F}{\pi}, \tag{A8b}$$
$$\psi_e(-L)=-\frac{2k_F^3L^2}{3\pi}+\frac{k_F^2L}{2}+\frac{\pi k_F}{6}. \tag{A8c}$$

From (3.7) we have for the background contribution

$$\psi_B(0)=0, \tag{A9a}$$
$$\psi_B(-L/2)=\frac{k_F^3L^2}{6\pi}-\frac{k_F^2L}{4}+\frac{3\pi k_F}{32}-\frac{\pi k_F}{12}, \tag{A9b}$$
$$\psi_B(-L)=\frac{2k_F^3L^2}{3\pi}-\frac{k_F^2L}{2}-\frac{\pi k_F}{6}. \tag{A9c}$$

Note that the last term of (A9b) and (A9c) is due to the order L^{-1} term in $a_\infty=3\pi/8k_F+\pi^2/8k_F^2L$. Terms of order L^2 and L are seen to cancel each other in the sum of (8) and (9), as they should. However, we find, in deviation from the familiar result,

$$\psi(0)=\psi(-L)=0, \tag{A10a}$$
$$\psi\left(\frac{-L}{2}\right)=-\frac{k_F}{\pi}+\frac{3\pi k_F}{32}-\frac{\pi k_F}{24}. \tag{A10b}$$

Most other derivations are considerably more elaborate, especially for the finite-barrier model. In this paper we have discussed them only in general terms. We feel that this simple example already provides insight in the nature of our results.

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