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Surface energy of jellium metal*

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A variational calculation is performed of the surface energy of the jellium model of a metal surface. Variational parameters are used which only affect the surface properties of the wave functions. The kinetic, electrostatic, and exchange energies are evaluated using these wave functions. The minimization procedure yields results very similar to those obtained by Lang and Kohn, and quite different from the infinite-barrier model.

I. INTRODUCTION

The surface energy of metals, in the jellium model, has been the subject of many recent investigations. The early calculations did not include the important contributions of correlation and exchange.[1,2] These were first included by Lang and Kohn, who used the local density approximation.[3,4] A different type of calculation was performed by Craig,[5,6] and Schmit and Lucas,[7] who independently suggested that the total surface energy could be explained by the zero-point energy of the plasmon modes. These two approaches are very different, and some controversy arose over the validity of the two methods. In the beginning, the main point of discussion centered about the magnitude of the correlation energy, since Lang and Kohn found it to be quite small while the other approach found it to be quite large. Later it was realized that this is inappropriate, and one should always, when comparing two theories, compare the sum of exchange plus correlation energy. A second point of disagreement between the two theories was the result of Lang and Kohn that the surface energy of jellium went negative at high electron density. This did not happen in the other theory. This negative energy largely arose from the kinetic-energy term.

A large number of theoretical calculations were reported which attempted to explain these differences, in particular the exchange and correlation part of the surface energy.[8–17] Most of these calculations employed a theoretical model called the infinite-barrier model.[11–14] The particles are assumed confined to a box of width L and infinite walls, so that the z component of the wave function is simply

$$\Psi_n(z) = (2/L)^{1/2} \sin(n\pi z/L) \quad .$$

The simplicity of these wave functions permits an exact computation of the surface exchange energy. This nonlocal computation is still quite difficult, but the result was reported by Harris and Jones.[14] The correlation energy in the random-phase approximation (RPA) was reported by Wikborg and Inglesfield.[13] These and related calculations seem to show that the zero-point energy of the plasmons makes only a small contribution to the surface energy. The local density calculation, which omits this contribution, thereby is a good approximation to the surface energy.

The surface energy is the sum of four terms: kinetic,[18] electrostatic, exchange, and correlation. Figure 1 shows these four energy contributions compared: the Lang-Kohn results versus those reported for the infinite-barrier model. Each theory gives quite different results for each energy term. The kinetic-energy term is quite significant—notice the scale change of a factor of 4 between it and the other curves—since Lang-Kohn report a large negative kinetic energy, while the infinite-barrier model is large and positive. The sum of the terms is dominated by the large kinetic-energy term, and the totals are very different for

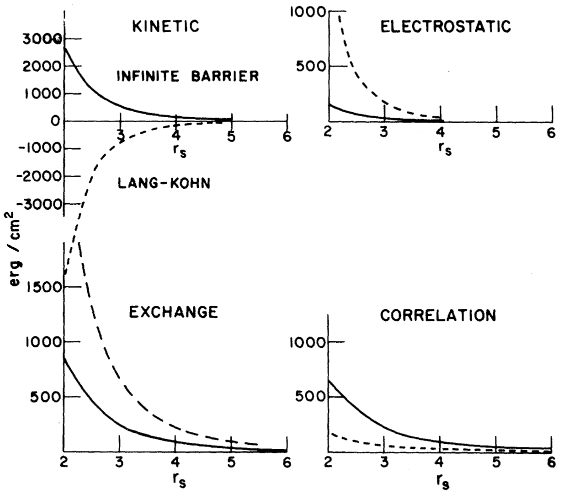

FIG. 1. Energy terms contributing to the surface energy of jellium metal. The dashed line is the result of Lang and Kohn (Ref. 3) using the local-density approximation. The solid lines are the results of nonlocal calculations using infinite-barrier wave functions. The exchange energy is from Harris and Jones (Ref. 14) and the correlation energy is from Wikborg and Inglesfield (Ref. 13).

the two models.

The calculations reported here were undertaken to understand the differences between these two theories. We simply wished to know which theory is more correct. Our results definitely suggest that the numbers reported by Lang-Kohn are better than those reported using the infinite-barrier model.

We did a variational calculation. A variational parameter λ was introduced into the wave function $\Psi_n(z, \lambda)$. This was chosen so that varying λ only affected the surface part of the wave function. The total energy for the N-particle system $E_T(\lambda)$ depends upon λ, but only in the surface part

$$E_T(\lambda) = NE^B + 2AE^S(\lambda) \ ,$$

where E^B is the bulk energy per particle. The metallic slab has two surfaces of area A. Hence varying λ only varies the surface energy, and a minimization of the total energy with respect to λ only minimizes the surface energy.

The wave functions are chosen so that for one value of λ we have the infinite-barrier model, while for another value we obtain results very similar to those of Lang-Kohn. The variational procedure clearly indicates a minimization at the values near those reported by Lang-Kohn. Thus our nonlocal calculation reproduces numerical results very similar to those of the local-density approximation. We only compute three of the energy terms: kinetic, electrostatic, and exchange. The correlation energy is not included, but we argue that its omission will not change our conclusion that the infinite-barrier model is a poor description of a surface.

We note that previous variational calculations have been reported on the surface properties of metals.[19,20] These have used the local-density approximation, while we are doing a nonlocal calculation.

II. VARIATIONAL CALCULATION

The electron wave functions used in the variational calculation were those for a finite barrier at the surface. With $Z=0$ at the center of the slab, the finite-barrier potential is

$$V(Z) = 0 \ , \quad |Z| \le L \ ,$$
$$V(Z) = V_0 \ , \quad |Z| \ge L \ .$$

The wave functions for this potential were given by Huntington[1] and Stratton.[2] Our variational parameter λ is the ratio of V_0 to the free-electron Fermi energy

$$\lambda = V_0/E_F \ . \tag{2.1}$$

The permissible values of λ range between one and infinity

$$1 \le \lambda < \infty \ .$$

The case $\lambda=\infty$ is the infinite-barrier model. The value $\lambda=1$ is a lower limit, since for values less than this, the electrons leak out of the crystal. All energy terms seem well behaved at the point $\lambda=1$.

Another parameter of the theory is the distance $d(\lambda)$ in the Z direction between the jellium edge and the finite-barrier potential. This distance is determined by the charge neutrality of the surface to be[2]

$$d(\lambda) = (3/4k_F)[\pi/2 - (2-\lambda)\sin^{-1}(\lambda^{-1/2}) - (\lambda-1)^{1/2}] \ . \tag{2.2}$$

Thus this is a dependent variable, and λ is the only free parameter of the theory.

It should be emphasized that we do not use the potential $V(Z)$ in our energy computations, nor assume that it exists. We use it only to generate a set of wave functions. Then we throw away the potential, and use the wave functions.

The first term we calculate is the kinetic energy of the surface. This is easily deduced from Huntington,[1]

$$\begin{aligned} E^S_{\mathrm{KE}} &= (\hbar^2 k_F^4/160\pi m)[1+h(\lambda)] \ , \\ h(\lambda) &= (1/2\pi)[(15\lambda^2 - 16\lambda - 8)\sin^{-1}(\lambda^{-1/2}) \\ &\quad + 3(2-5\lambda)(\lambda-1)^{1/2}] \ , \end{aligned} \tag{2.3}$$

although he did not give it explicity. Since $h(\infty)=0$, the first term is the infinite-barrier result, while $h(\lambda)$ gives the correction for the finite barrier. At $\lambda=1$ the value is

$$h(1) = -\tfrac{9}{4} \ .$$

Thus varying λ within its permissible range makes the kinetic-energy term go from very positive to very negative. The kinetic energy is the only term with a strong λ dependence. The minimization of the surface energy tends to occur where the kinetic-energy contribution is lowest, which is near $\lambda=1$. The result (2.3) may be written in atomic units [Ry/(Bohr radius)^2] as

$$\begin{aligned} E^S_{\mathrm{KE}} &= A(\lambda)/r_s^4 \ , \\ A(\lambda) &= 0.0540[1+h(\lambda)] \ . \end{aligned} \tag{2.4}$$

The second term is the electrostatic energy. The electron density near one edge is given by

$$\begin{aligned} n(z) &= 3n_0 \int_0^1 dx\,(1-x^2)\,\phi(x,z) \ , \\ \phi(x,z) &= x^2 \exp[2y(\lambda - x^2)^{1/2}]/\lambda \ , \quad y<0 \ , \\ \phi(x,z) &= \sin^2[xy + \sin^{-1}(x/\lambda^{1/2})] \ , \quad y>0 \ , \\ y &= k_F[Z + d(\lambda)] \ , \end{aligned} \tag{2.5}$$

where $x=k/k_F$, and n_0 is the bulk density. The point $Z=0$ refers to the jellium edge and $y=0$ to the step barrier edge. This density was calculated numerically. Then the electrostatic energy of a single surface is

$$E^S_{\mathrm{ES}} = 2\pi e^2 \int_{-\infty}^{\infty} dz\,[n(z) - n_0\theta(z)] \int_{-\infty}^{z} dz' \times (z' - z)[n(z') - n_0\theta(z')] \; .$$

In atomic units, this may be written

$$E^S_{\mathrm{ES}} = B(\lambda)/r_s^3 \; , \tag{2.6}$$

where the result for the infinite-barrier model is

$$B(\infty) = 0.001\,56 \; .$$

The third term is the exchange energy. Our nonlocal calculation used the numerical method developed by Harris and Jones[14] for the infinite-barrier model. The method is to begin with the standard formula for the total exchange energy

$$E^T_{\mathrm{Ex}} = -\frac{e^2}{4} \int \frac{d^3r\,d^3r'}{|r - r'|} F(r, r')^2 \; ,$$
$$F(r, r') = 2 \sum_{n, k_{\|}} \Psi_{n, k_{\|}}(r)\,\Psi_{n, k_{\|}}(r') \; , \tag{2.7}$$

and extract from it a volume term and a surface term

$$E^T_{\mathrm{Ex}} = n_0\,\Omega\,E^B_{\mathrm{Ex}} + 2A\,E^S_{\mathrm{Ex}} \; ,$$
$$E^B_{\mathrm{Ex}} = -\,3e^2 k_F/4\pi \; , \quad \Omega = 2A[L - d(\lambda)] \; ,$$

where Ω is the volume of the jellium. After doing the (x, y) integrals in (2.7) one obtains

$$E^T_{\mathrm{Ex}} = -\frac{2\pi e^2}{A} \sum_{\substack{k_{\|}, k'_{\|} \\ n, n'}} \theta(\epsilon_F - \epsilon_{k_{\|}, n})\,\theta(\epsilon_F - \epsilon_{k'_{\|}, n'})\,G(q, n, n') \; ,$$
$$G(q, n, n') = \frac{1}{q} \int_{-\infty}^{\infty} dz \int_{-\infty}^{\infty} dz'\, e^{-q|z-z'|}\,\phi_n(z) \times \phi_n(z')\,\phi_{n'}(z)\,\phi_{n'}(z') \; , \tag{2.8}$$

where $\phi_n(z)$ are the Z part of the wave function for the finite slab, and n is the discrete quantum number. The z integration in (2.8) yields a very lengthy result for $G(q, n, n')$, from which one can extract the volume and surface terms. The surface contribution to the exchange energy is numerically integrated using the method of Harris and Jones. The result may be written in atomic units as

$$E^S_{\mathrm{Ex}} = C(\lambda)/r_s^3 \; ,$$
$$C(\infty) = 0.008\,66 \; .$$

The correlation energy is defined as all other contributions to the energy, beyond the three which have been mentioned. In perturbation theory, this is an infinite series of terms, which cannot be evaluated exactly. Recent calculations using infinite-barrier wave functions have solved the surface correlation energy in the random-phase approximation.[11-14] This appears to be prohibitively difficult with our wave functions which are more complicated. We finally abandoned the idea of computing the correlation energy because of the numerical difficulties. The omission of this term severely limits the accuracy of our energy calculation. It is possible that the calculated correlation energy might be small. This is based upon the observation that Lang and Kohn found it to be small, and of our other three energy terms come out to be very similar to theirs. However, this is just a speculation, and we do not know whether the surface correlation energy is small.

III. NUMERICAL RESULTS

The electron density we calculate is shown in Fig. 2 for $\lambda = 1$ and $\lambda = \infty$. These two results differ little from each other. The most significant difference is the long tail for negative Z which characterizes $\lambda = 1$. The triangular points are the Lang-Kohn results for $r_s = 4$. These agree remarkably well with our results for $\lambda = 1$.

One of the standard justifications for the infinite-barrier model is that it predicts a density profile at the surface which is similar to those found by Lang and Kohn. Figure 2 shows that this is indeed the case. However, in Fig. 1 we showed that the infinite-barrier model predicts all energy terms to be quite different than those found by Lang and Kohn. Thus slight differences in surface density profile have a large effect upon the energy terms.

Figure 3 shows the λ dependence of $A(\lambda)$, $B(\lambda)$, and $C(\lambda)$, which are the coefficients of the kinetic, electrostatic, and exchange energies. The two Coulomb energies are hardly affected by λ, and only vary near $\lambda = 1$. This variation is only on the scale of a factor of 2. The kinetic energy, as remarked earlier, has a steady and spectacular λ

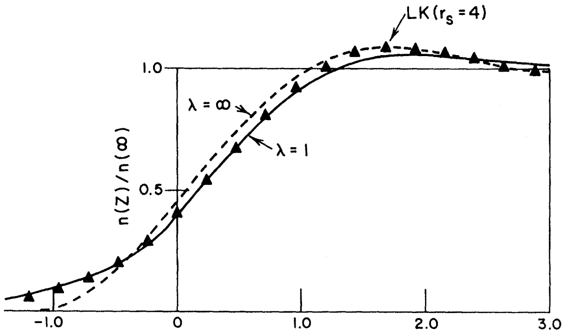

FIG. 2. Electron density at the surface, compared for the infinite-barrier model ($\lambda = \infty$) and the finite-barrier model ($\lambda = 1$). The traingles give the Lang-Kohn profile for $r_s = 4$. The three curves are similar, although the Lang-Kohn result is more like $\lambda = 1$ result than $\lambda = \infty$. The jellium edge is at $Z = 0$.

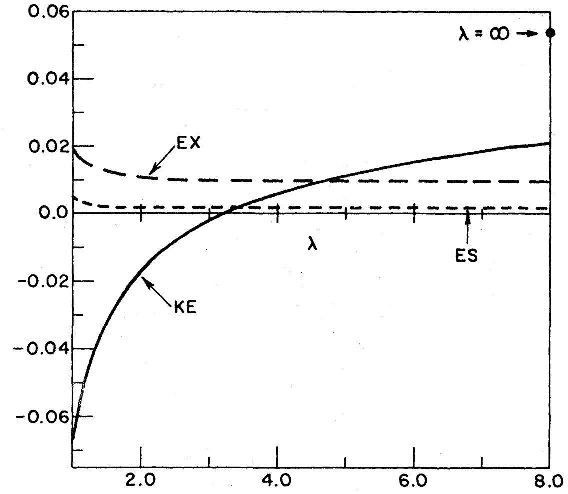

FIG. 3. λ dependence of the three coefficients $A(\lambda)$, $B(\lambda)$, and $C(\lambda)$ for the kinetic, electrostatic, and exchange energies. The point $\lambda=\infty$ on the upper right is the asymptotic limit of the kinetic energy.

dependence, since it goes from very positive to very negative.

For each value of density (r_s) we vary λ and find the minimum of the total energy

$$E^S(\lambda)=[A(\lambda)/r_s+B(\lambda)+C(\lambda)]/r_s^3 \ .$$

The energy curve for $r_s=5$ is shown in Fig. 4. The minimum occurs at $\lambda_0=1.30$. For λ values higher than this the kinetic energy increases, while for λ values lower the Coulomb terms increase. λ_0 decreases with decreasing r_s, and reaches $\lambda_0=1$ about $r_s=3$. For lower values of r_s the minimization occurs just at $\lambda_0=1$. For each value of r_s, the three energy terms are evaluated at λ_0. These results are shown in Fig. 5, which compares these results to those of Lang and Kohn, and the infinite-barrier model.

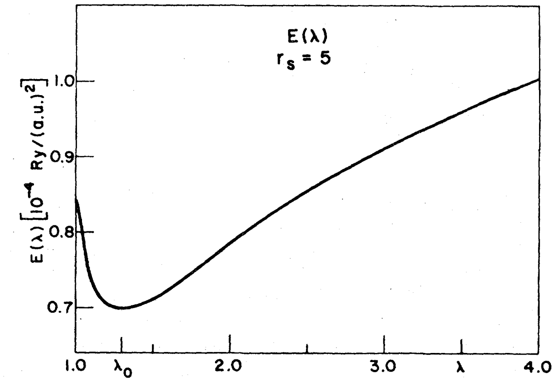

FIG. 4. Minimization curve for $r_s=5$.

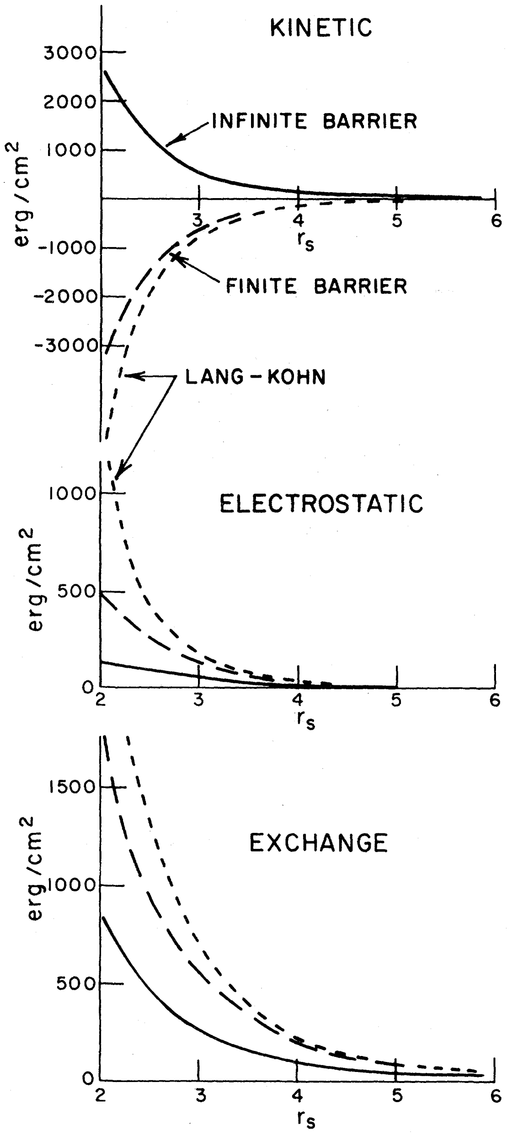

FIG. 5. Results for the variational procedure for the finite barrier are compared with the other two theories. The variational theory (long dashed line) gives results very similar to Lang and Kohn for the two largest terms: kinetic and exchange.

The variational procedure produces results similar to those of Lang and Kohn. The kinetic energy is large and negative. The electrostatic term is midway in value between the two models, but this is a small term and less significant than the others. The exchange energy is larger than the infinite barrier model, and similar to that obtained by Lang and Kohn.

IV. DISCUSSION

The main results of this paper are two conclusions. First, the infinite barrier model provides a poor description of a jellium surface. This conclusion is relevant because much recent and present theoretical work on surface properties of metals employs this model. It appears to predict substantially incorrect properties, and results from it are not to be trusted. This point is also made in Ref. 19.

Our second conclusion is that the local density approximation is quite good. Our nonlocal calculations using wave functions predict results similar to those found in the local density approximation. We suspect that this agreement could be improved if we were to improve our calculation: either by including correlation or a better choice of variational function.

The accuracy of our result suffers from the omission of correlation energies. But we do not think this omission affects either of the two conclusions above. The minimization procedure is dominated by the large λ dependence of the kinetic-energy term. This forces $E^s(\lambda)$ to minimize at a λ_0 near one. We regard it as unlikely that the correlation energy changes this. This hypothesis is based largely on the fact that the correlation energy is a Coulomb term, and the other Coulomb terms are insensitive to λ except at very low values.

We also considered replacing the jellium background by a discrete lattice of finite ions. This could be done using a pseudopotential for the ion potential, and treating the ion effects classically—in the manner of Lang and Kohn. We decided against doing it, since the answers would come out similar to theirs. This is because the result depends only upon charge density, and Fig. 2 shows that our charge densities are almost identical to theirs.

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