PHYSICAL REVIEW B VOLUME 15, NUMBER 4 15 FEBRUARY 1977

Metal surface properties in the linear potential approximation

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(Received 29 June 1976)

Jellium metal surface properties including the dipole barrier, work function, and surface energy are obtained in the linear-potential approximation to the effective potential at the surface. The metal surface position and field strength are determined, respectively, by the requirement of overall charge neutrality and the **constraint** set on the electrostatic potential by the Budd-Vannimenus theorem. The surface energies are obtained both within the local density approximation and by application of a sum rule due to Vannimenus and Budd, and the two methods compared. The calculations are primarily analytic and all properties, with the exception of the exchange-correlation energy, are given in terms of universal functions of the field strength. The effects of correlation on the various properties are studied by employing three different approximations for the correlation energy per particle. The results obtained employing the Wigner expression for the correlation energy closely approximate those of Lang and Kohn. The use of different correlation functions, however, leads to only small differences in the results for the dipole barrier, work function, and the exchange-correlation contribution to the energy, but the results for the total surface energy are significantly different.

I. INTRODUCTION

In this paper we present the results of a model potential calculation of jellium metal[1] surface properties. The principal advantage of such model calculations[2,3] is the elimination of the requirement of a numerical solution of the Schrödinger equation for particles moving in a self-consistently obtained effective potential which is intrinsic to other more complex formalisms.[4,5] Together with the application of certain theoretical constraints, which help to fully define the model effective potential, it is then possible to determine various properties of interest, such as work functions and surface energies. Examples of typical constraints applicable to model metal surface calculations are the requirement of self-consistency of the surface dipole barrier,[2] the condition on the electrostatic potential at the metal surface set by the Budd-Vannimenus theorem[6] (BVT), and the Rayleigh-Ritz[7] energy minimum criteria, in addition to the charge neutrality condition.[8] The choice and number of these constraints to be satisfied would, of course, depend upon the complexity of the model potential employed.

We consider here the linear potential model[9,10] approximation to the effective potential at a metal surface (see Fig. 1). For a given value of the field strength, the metal surface position is fixed by requiring overall charge neutrality. The field strength may then be determined by application of the BVT. The choice of the BVT criteria as the constraint is governed by the fact that its application in our previous work[2,3] consistently led to good results for both the work function and surface energy rather than, for example, just the latter, as is the case[3] on application of the variational principle for the energy. In Sec. II we give a discussion of the calculations, and definitions of properties and theorems employed. The results for the surface dipole barrier, work function, and surface energies are presented in Sec. III. The surface energies are determined both within the local-density approximation (LDA), which is meaningful provided both exchange and correlation are treated locally,[11,12] and by application of a sum rule due to Vannimenus and Budd. The use of the Vannimenus-Budd theorem[13] (VBT) appears particularly attractive, as it completely eliminates the requirement of determining the individual components of the energy and any questions regarding the accuracy of the LDA,[11,14,15] and the effects of inclusion of the gradient terms.[4] These sets of results thus afford a comparison[3]

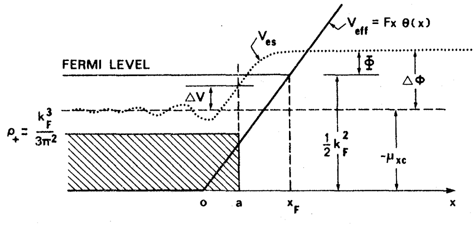

FIG. 1. Schematic representation of the linear potential model of a metal surface indicating all relevant energies. The hatched region represents the uniform positive background beginning at the metal surface.

of the two methods for obtaining metal surface energies. In order to study the effects of correlation on the various surface properties, we have also employed three different correlation functions due to Wigner,[16] Pines and Nozières,[17] and Vashista and Singwi,[18] in our calculations. The correlation energy per particle as given by these expressions can differ by as much as twenty percent for low-density metals. Finally, we compare our results obtained by employing the Wigner approximation for correlation with those of the self-consistent calculations of Lang and Kohn[5] (LK).

II. CALCULATION OF METAL SURFACE PROPERTIES

In this model calculation, the effective potential $V_{\text{eff}}(x)$ at a metal surface (see Fig. 1) is assumed to be

$$V_{\text{eff}}(x) = Fx\Theta(x), \tag{1}$$

where F is the field strength defined in terms of the slope parameter x_F as $F = k_F^2/2x_F$, $\frac{1}{2}k_F^2$ is the Fermi energy,[19] and $\Theta(x)$ is the step function. The electronic wave function $\psi_k(x)$ for $x \leqslant 0$ is given as

$$\psi_k(x) = -(2/L)^{1/2}\sin[kx + \delta(k)]. \tag{2}$$

In the region $x \geqslant 0$, the Schrödinger equation is the Airy differential equation[20,21]

$$\frac{d^2\psi_k}{d\zeta^2} - \zeta\psi_k = 0, \tag{3}$$

whose solution is

$$\psi_k(\zeta) = C_k \mathrm{Ai}(\zeta), \tag{4}$$

where $\mathrm{Ai}(\zeta)$ is the Airy function, C_k is a normalization factor, $\zeta = (x - E/F)(2F)^{1/3}$, and E is the energy. The factor C_k and the phase shift $\delta(k)$ are determined by the requirement of the continuity of the wave function and its logarithmic derivative at the origin. Thus,

$$C_k = -(2/L)^{1/2}\sin\delta(k, x_F)[\mathrm{Ai}(-\zeta_0)]^{-1} \tag{5}$$

and

$$\cot\delta(k, x_F) = \frac{1}{(\zeta_0)^{1/2}}\,\frac{\mathrm{Ai}'(-\zeta_0)}{\mathrm{Ai}(-\zeta_0)}, \tag{6}$$

where $\zeta_0 = (k^2/k_F^2)(k_F x_F)^{2/3}$, and where $\mathrm{Ai}'(\zeta)$ is the derivative of the Airy function.

The fundamental quantities from which all other surface properties may be obtained are the electronic and total charge densities defined as

$$\rho_e(x) = \frac{L}{2\pi^2}\int_0^{k_F} (k_F^2 - k^2)|\psi_k|^2\,dk \tag{7}$$

and

$$\rho_T(x) = \rho_e(x) - (k_F^3/3\pi^2)\Theta(-x + a), \tag{8}$$

respectively. Implicit in the definition of the total charge density is the assumption that the positive ions of the metal are smeared out and replaced by a uniform charge background of density $\rho_+ = k_F^3/3\pi^2$ ending abruptly at the metal surface position at $x = a$.

The surface dipole barrier contribution to the work function is given by the expression

$$\Delta\phi = 4\pi\int_{-\infty}^{+\infty} x\rho_T(x)\,dx. \tag{9}$$

The electrostatic potential $V_{\text{es}}(x)$ required for application of the BVT, VBT, and the electrostatic contribution to the surface energy is obtained by solution of Poisson's equation

$$\frac{d^2V_{\text{es}}}{dx^2} = -4\pi\rho_T(x), \tag{10}$$

with the boundary conditions $V_{\text{es}}(-\infty) = V'_{\text{es}}(-\infty) = 0$. Applying the charge neutrality condition, the electrostatic potential may thus be written

$$V_{\text{es}}(x) = \Delta\phi - 4\pi\int_{\infty}^{x} dx'\int_{\infty}^{x'} dx''\rho_T(x''). \tag{11}$$

The surface energy of a metal E_s which is the energy required to split the crystal in two along a plane may be obtained from the sum of the kinetic, electrostatic, exhange and correlation contributions. The kinetic energy E_k is given as[1,10]

$$E_k = E_k^{(1)} - E_k^{(2)}, \tag{12}$$

where

$$E_k^{(1)} = (k_F^4/160\pi)\Theta,$$
$$\Theta = 1 + \frac{80}{\pi k_F^4}\left(\tfrac{3}{5}k_F^2\int_0^{k_F} k\delta(k)\,dk - \int_0^{k_F} k^3\delta(k)\,dk\right) \tag{13}$$

and

$$E_k^{(2)} = \int_{-\infty}^{+\infty} (V_{\text{eff}}[\rho_e; x] - V_{\text{eff}}[\rho_e; -\infty])\rho_e(x)\,dx. \tag{14}$$

The electrostatic contribution to the surface energy E_{es} is

$$E_{\text{es}} = \tfrac{1}{2}\int_{-\infty}^{+\infty} \rho_T(x)V_{\text{es}}(x)\,dx, \tag{15}$$

and the sum of the exchange and correlation contributions E_{xc} which must be taken together within the LDA is given as[1]

$$E_{xc} = \int_{-\infty}^{+\infty} [\epsilon_{xc}(\rho_e(x)) - \epsilon_{xc}(\bar{\rho}_e)]\rho_e(x)\,dx, \tag{16}$$

where $\epsilon_{xc} = \epsilon_x + \epsilon_c$, ϵ_x, and ϵ_c are the average exchange and correlation energies per particle for a uniform electron gas, and where $\bar{\rho}_e = k_F^3/3\pi^2$ is the mean interior electronic density.

The expression for the derivative of the surface energy with respect to the Wigner-Seitz radius r_s which according to the VBT is given as[13]

$$\frac{dE_s}{dr_s} = -\frac{9}{4\pi r_s^4}\int_{-\infty}^{a}\left[V_{es}(-\infty) - V_{es}(x)\right]dx, \tag{17}$$

may also be employed to obtain the surface energy directly by integration over r_s, together with a suitable choice for the constant of integration.

In this model the two variable parameters are the metal surface position a and the field strength F. For a given F the metal surface position may be determined either by the charge neutrality condition

$$\int_{-\infty}^{+\infty}\rho_T(x)\,dx = 0\ , \tag{18}$$

or by application of the phase-shift rule of Sugiyama,[10] according to which

$$a = -\frac{3\pi}{8k_F} - \frac{3}{k_F^3}\int_0^{k_F} k\delta(k)\,dk. \tag{19}$$

The field strength, or equivalently, the slope parameter x_F is adjusted so as to satisfy the requirement set on the electrostatic potential by the BVT such that[6]

$$\Delta V = V_{es}(a) - V_{es}(-\infty) = \rho_e\frac{d\epsilon_T}{d\rho_e}, \tag{20}$$

where ϵ_T is the sum of the kinetic, exchange, and correlation energies per particle for a uniform electron gas.

With the transformation $y = k_F x$, and $k/k_F = q$, such that the metal surface position is now defined to be at $y_a = k_F a$, it can be shown that the quantities y_a, ρ_e/k_F^3, $\Delta\phi/k_F$, V_{es}/k_F, E_k/k_F^4, E_{es}/k_F^3, and $r_s^4\,dE_s/dr_s$ are all universal functions of the slope parameter $y_F = k_F x_F$. Furthermore, all the spatial integrals in the expressions for the metal surface position, the surface dipole barrier, the electrostatic potential, and the kinetic energy can be done analytically. Thus, together with the electronic density, the determination of these properties reduces to a simple numerical calculation of k-space integrals ranging from 0 to 1. The explicit expressions employed in the present calculations are given in the Appendix. Plots of the universal functions y_a, $\Delta\phi/k_F$, $160\pi E_k/k_F^4$, E_{es}/k_F^3, and $(\frac{4}{9}\pi)r_s^4\,dE_s/dr_s$ are given in Figs. 2–6. The metal surface position, surface dipole barrier, and surface energies are then easily determined for a specific metal [defined by its Fermi momentum $k_F = 1/\alpha r_s$; $\alpha^{-1} = (\frac{9}{4}\pi)^{1/3}$] by adjusting the slope parameter x_F till it satisfies the BVT.

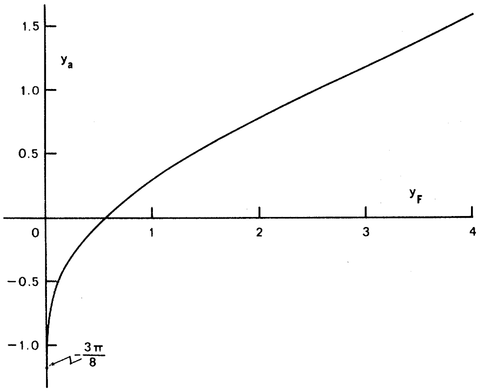

FIG. 2. Plot of the universal function for the metal surface position y_a vs the slope parameter y_F.

The work function of the metal Φ is then given as

$$\Phi = \Delta\phi - \tfrac{1}{2}k_F^2 - \mu_{xc}\,, \tag{21}$$

where μ_{xc} is the exchange and correlation part of the chemical potential of a uniform electron gas defined as

$$\mu_{xc} = \frac{d(\rho_e\,\epsilon_{xc})}{d\rho_e}\,. \tag{22}$$

The exchange energy[22] per particle for the uniform electron gas is $\epsilon_x = -0.458/r_s$. For the correlation energy per particle valid at metallic densities we employ the correlation functions[19] due to Wigner[16] (W), Pines and Nozières[17] (PN), and Vashista and Singwi[18] (VS),

$$\epsilon_c^{W} = -0.44/(r_s + 7.8),$$
$$\epsilon_c^{PN} = 0.0155\ln r_s - 0.0575,$$
$$\epsilon_c^{VS} = 0.01675\ln r_s - 0.056.$$

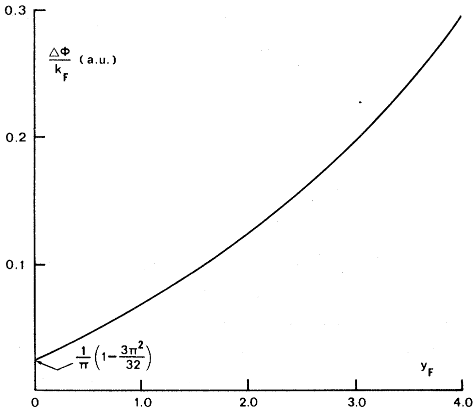

FIG. 3. Plot of the universal function $\Delta\phi/k_F$, where $\Delta\phi$ is the surface dipole barrier, vs the slope parameter y_F.

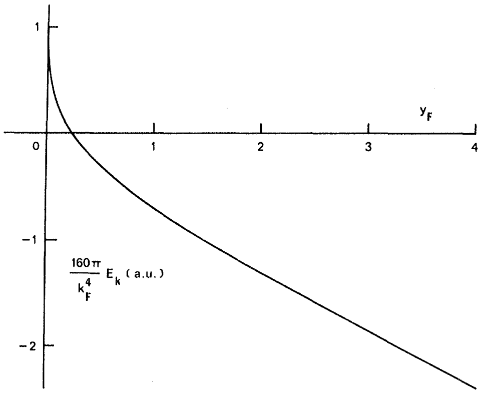

FIG. 4. Plot of the universal function $(160\pi/k_F^4)E_k$, where E_k is the kinetic energy, vs the slope parameter y_F.

Although the VS and PN expressions are similar, their respective values for ϵ_c can differ by as much as 15% for $r_s = 6$, for which value of r_s the VS expression differs by 20% from that due to Wigner. The results for the various properties within the linear potential model employing these different correlation functions are presented in Sec. III.

III. RESULTS

A. Surface dipole barrier and work functions

In Table I we present the results for the surface dipole barrier and work function for the three different correlation functions. For $r_s = 2-4$, both the BVT and charge neutrality are exactly satisfied, whereas for $r_s \geqslant 4.5$, no choice of parameters in the linear potential model satisfy both these requirements. Thus for $r_s \geqslant 4.5$, the present work corresponds to satisfying the BVT as closely as possible in the limit of this model, i.e., by a potential of infinite slope, and by the charge neutrality condition.

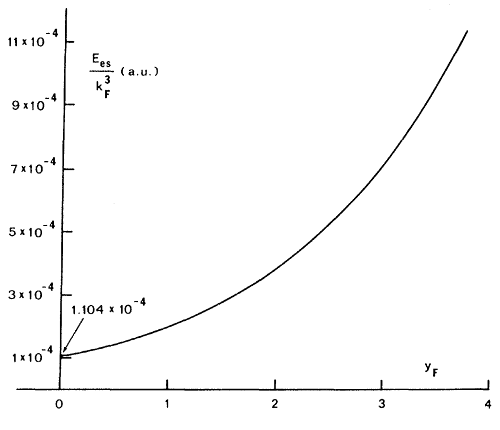

FIG. 5. Plot of the universal function E_{es}/k_F^3, where E_{es} is the electrostatic energy, vs the slope parameter y_F.

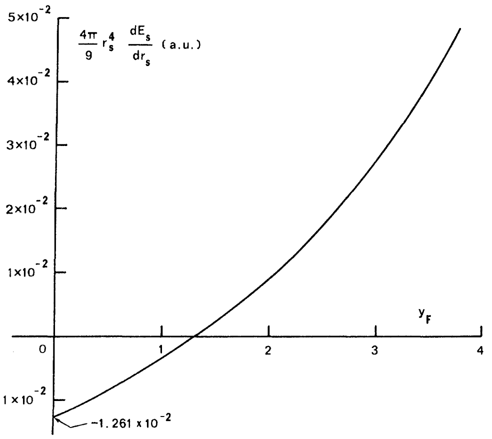

FIG. 6. Plot of the universal function $(\frac{4}{9}\pi)r_s^4\, dE_s/dr_s$, where E_s is the surface energy, vs the slope parameter y_F.

A comparison of the Wigner (W) results with those of LK indicate that the model reproduces the large dipole moments required for high-density metals, differing by 0.23, 0.04, and 0.19 eV for $r_s = 2.0$, 2.5, and 3.0, respectively. The reason for the accuracy of these results is that by adjusting ΔV so as to satisfy the BVT, one has already obtained approximately 40% of the dipole barrier, exactly. The remaining contribution to $\Delta\phi$ from charge outside the metal is determined accurately since the model permits a large electronic spillover. In addition, satisfaction of the BVT also leads to very accurate electronic densities in this range. For $r_s = 3.5$ and 4.0, the model becomes progressively more reflecting as the potential rises more steeply leading to underestimates for the dipole barrier. Also, ΔV in this range comprises only about 25% of the LK value. For $r_s \geqslant 4.5$, for which the contribution of the dipole barrier to the work function is small, the results for $\Delta\phi$ are within 0.28 eV of those obtained by LK. In this range, the LK results[6] also do not satisfy the BVT, although their results more closely satisfy this condition than do the results of the infinite barrier model.[2] Thus over the entire metallic range the results of this model calculation for the dipole barrier and work function are within 0.32 eV of those due to LK.

The use of the PN and VS correlation functions lead to results for $\Delta\phi$ and Φ which are consistently lower than those obtained employing the W function. The PN and VS results for $\Delta\phi$ are within 0.03 eV of each other, the VS result dif-

TABLE I. Results for the surface dipole barrier $\Delta\phi$ and work function Φ for the correlation functions due to Wigner (W), Pines and Nozières (PN) and Vashista and Singwi (VS). The values for the metal surface position y_a and slope parameter y_F quoted are those obtained using the Wigner expression for the correlation energy.

r_s	$y_F=k_Fx_F$	$y_a=k_Fa$	Surface dipole barrier $\Delta\phi$ (eV)				Work function Φ (eV)				$\|\Phi_{LK}-\Phi\|$ (eV)
			Present work			Lang-Kohn [a]	Present work			Lang-Kohn [a]	
	W	W	W	PN	VS	W	W	PN	VS	W	W
2.0	3.760	1.488	7.03	6.90	6.88	6.80	4.12	4.09	4.02	3.89	0.23
2.5	2.801	1.108	3.79	3.69	3.66	3.83	3.68	3.63	3.55	3.72	0.04
3.0	1.967	0.763	2.13	2.05	2.02	2.32	3.31	3.26	3.17	3.50	0.19
3.5	1.214	0.410	1.18	1.12	1.09	1.43	3.01	2.95	2.85	3.26	0.25
4.0	0.507	−0.0370	0.59	0.53	0.50	0.91	2.74	2.68	2.57	3.06	0.32
4.5	0.000	−1.178	0.28	0.28	0.28	0.56	2.59	2.57	2.49	2.87	0.28
5.0	0.000	−1.178	0.25	0.25	0.25	0.35	2.63	2.60	2.51	2.73	0.10
5.5	0.000	−1.178	0.23	0.23	0.23	0.16	2.61	2.58	2.49	2.54	0.07
6.0	0.000	−1.178	0.21	0.21	0.21	0.04	2.58	2.54	2.45	2.41	0.17

[a] See Ref. 5.

fering by at most 0.15 eV from the W result. On the other hand, it is the PN and W values for Φ which are more similar, being within 0.06 eV of each other, the VS and W results differing by a maximum of 0.17 eV. Thus these different correlation functions give rise to only small differences in the results for the dipole barrier and work function. Since our results are close to those of LK using the W correlation function, we expect that a completely self-consistent calculation employing the other correlation functions would differ from LK by similarly small amounts, i.e., of the order of 0.1 or 0.2 eV.

B. Surface energies–local density approximation

In Table II we present the results for the surface energy for the three different correlation functions determined in the LDA. The parameters employed are the same as those of Table I obtained by satisfying the BVT and charge neutrality conditions, and the results given only for those values of r_s for which both these conditions are exactly satisfied, viz, $r_s=2-4$. The use of the infinite barrier model for $r_s \geq 4.5$ leads to unrealistic results within the LDA, due primarily to the sensitivity of this method of computing energies to the vanishing of the electronic density at the artificial barrier.[3] Other methods however, such as the VBT employing the same model do lead to meaningful results for these low densities, as discussed in Ref. 3. We have also included in Table II the results for the infinite barrier model for $r_s=2-4$.

A study of Table II indicates that the results for the total energy of the W column closely approximate those due to LK (see also Fig. 7). For $r_s=2-3$, the results for the individual components are also close approximations, the accuracy of the electronic densities being particularly well reflected in the results for the kinetic and exchange-correlation energies. Since for $r_s=3.5$

TABLE II. Surface energies in ergs/cm^2 as obtained in the local density approximation for the different correlation functions due to Wigner (W), Pines and Nozières (PN), and Vashista and Singwi (VS). The individual component values correspond to the Wigner expression for the correlation energy.

r_s	Surface energy components (Wigner correlation function) Present work			Surface energies E_s				
				Infinite Barrier Potential [a]	Present work			Lang-Kohn [b]
	E_k	E_{xc}	E_{es}		W	PN	VS	W
2.0	−5897	3386	1567	4077	−944	−863	−843	−1008
2.5	−1861	1458	447	1832	44	80	92	36
3.0	−666	718	153	964	205	223	231	199
3.5	−236	383	59	565	206	218	224	194
4.0	−51	213	23	359	185	201	208	158

[a] See Ref. 3.

[b] See Ref. 5.

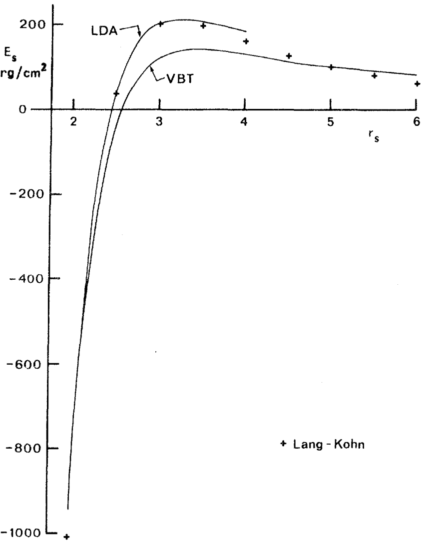

FIG. 7. Comparison of the surface energies obtained within the local density approximation (LDA), and by application of the Vannimenus-Budd theorem (VBT), employing the Wigner expression for correlation. The crosses represent the results of Lang and Kohn.

and 4.0, the effective potential rises too steeply, the results for E_k are larger and those for E_{es} and E_{xc} smaller than the corresponding values obtained by LK. However, as was the case[3] for the step and infinite barrier models, the exchange-correlation energies for all values of r_s are considerably more accurately obtained than either the kinetic or electrostatic contributions. For example, for $r_s = 2.5$, E_{xc} differs by 0.06%, whereas E_k and E_{es} differ by 0.6% and 4%, respectively, from those of the results of LK. These results together with those of the other models studied indicate that E_{xc} as obtained in the LDA is quite insensitive to changes in the effective potential, in sharp contrast to the kinetic energy. In fact it can be shown by expanding E_{xc} about the exact density that the error in the calculated E_{xc} is proportional to the error in the calculated dipole moment which, in this model, is small. Thus, by permitting the infinite barrier to become a ramp, the results for the total energy are drastically altered, as may be observed by comparing the results of the infinite and linear potentials given in Table II.

The surface energies obtained by employing the PN and VS correlation functions may be observed to be significantly different from those obtained using the Wigner expression. These differences arise primarily due to the numerical differences in the values for the kinetic energy, and to a far lesser degree, from the differences in the electrostatic energy. The exchange-correlation energy for both the PN and VS results, on the other hand, are within 2% of those of the Wigner column. Thus, although the different correlation functions affect the total energy implicitly, via ΔV and thus E_k, their explicit contribution taken together with exchange is approximately the same.

C. Surface energies—Use of the Vannimenus-Budd theorem

In this subsection we present results (see Table III) for the derivative of the surface energy with respect to the Wigner-Seitz radius and the surface energy, as obtained by the sum rule of Vannimenus and Budd. The parameters are again chosen such that the BVT is either exactly satisfied, which is the case for $r_s \leqslant 4.3$, or as closely approximated as possible, as by the infinite barrier model for $r_s > 4.3$. An analytic expression for the derivative of the energy for the in-

TABLE III. Derivative of the surface energy with respect to the Wigner-Seitz radius dE_s/dr_s, and surface energies in ergs/cm^2, as obtained by application of the Vannimenus-Budd theorem employing the Wigner approximation for correlation.

	$\frac{dE_s}{dr_s}$		E_s	
r_s	Present work	Lang-Kohn[a]	Present work	Lang-Kohn[a]
2.0	3365	4447	−868	−980
2.5	669	755	−41	49
3.0	119	79	123	197
3.5	−9	−54	143	191
4.0	−36	−71	130	157
4.5	−34	−67	111	122
5.0	−23	−34	97.5	97.5
5.5	−15	−37	88	80
6.0	−11	−33	82	62

[a] See Ref. 13.

finite barrier model obtained from Eq. 17 is given in Ref. 3, and a plot of dE_s/dr_s over the entire metallic range is given in Fig. 8. The crosses in the figure represent the values obtained by Vannimenus and Budd employing the electrostatic potential of LK. The surface energy is determined by integration over r_s with the constant of integration[13] chosen such that the energy matches the LK value at $r_s = 5$. Although we could determine this constant by a physical criterion such as the $r_s \to \infty$ limit for which case the surface energy vanishes, we restrict ourselves to the above choice in order to enable comparisons with the work of Vannimenus and Budd. A graph of the surface energies thus obtained is also plotted in Fig. 7.

We note that for high densities, in contrast[3] to both the step and infinite potential models, the present model does permit dE_s/dr_s to become positive and large. However, although the graph for the derivative appears very similar to the LK results, a comparison of the explicit values given in Table III indicate them to be quite different. This is interesting because use of the LDA within this model with the same choice of parameters leads to very accurate surface energies. Since the LDA method depends primarily on the electronic density, and the VBT method on the total charge density inside the metal, the reason for the differences in the results of the two methods becomes evident on a comparison of the electronic and total charge densities and electrostatic potentials obtained with those of LK. Inside the metal, for example, the electronic density normalized with respect to the bulk value for $r_s = 2$ is within 4% of the LK density, differing by less than a percent in the range from -1.2 to -0.275 Fermi wavelengths. On the other hand, the total charge density near and at the metal surface can differ by as much as 30%. The major contribution to the integral of Eq. 17 for dE_s/dr_s arises from a region extending from the surface to approximately a third of a Fermi wavelength inside the metal. In this range, the results for the electrostatic potential differs by (6–9)% from those of LK. Furthermore, inside the metal, however, the differences in V_{es} are comparable to those of the electronic density. Thus it is these differences in total density, and hence V_{es} inside the metal which lead to the differences in the derivative of the surface energy and to its integral, i.e., the surface energy. The adjustment of the electrostatic potential such that it corresponds to the exact value at one point, viz., at the metal surface, cannot be expected to lead to precise values elsewhere. However, the results for the surface energy, though not as accurate as those of the LDA calculation, are fair approximations to the LK values, and meaningful over the entire metallic range (see Fig. 7). Thus a study of this more accurate model reaffirms the conclusion[3] that the VBT method for obtaining surface energies is particularly sensitive to the choice of effective potential.

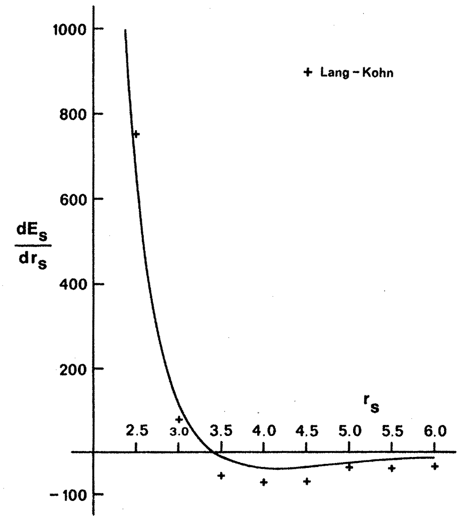

FIG. 8. Plot of the derivative of the surface energy E_s with respect to the Wigner-Seitz radius r_s vs r_s for the Wigner expression for correlation. The crosses represent the results obtained by Vannimenus and Budd employing the electrostatic potentials of Lang and Kohn.

We observe, in conclusion, that the linear potential model together with the constraint of the sum rule due to Budd and Vannimenus leads to results for all surface properties comparable to those obtained by Lang and Kohn for jellium metal. The fact that the effective potential does not become constant but increases indefinitely is unimportant, since the effective potential is in substantial error only in the region far from the metal surface where the electron density has exponentially decayed to a small fraction of its value at the surface. The majority of the calculations, as shown in the Appendix, are primarily analytic, and the universal curves permit a direct determination of surface properties on application of any theoretical constraint. Furthermore, due to the accuracy of the results and semianalytic nature of the density, it is reasonable to employ this model in order to study the effects of the gradient and higher-order terms on the exchange and correlation energies, and such an investigation is in progress. We also observe that although the LDA and VBT methods for obtaining energies lead to good results in comparison with those of Lang and Kohn, the former method proves to be superior, and it would thus be of interest to determine how the results of the two methods compare on inclusion of the gradient term contribution to the existing LDA value. Finally, we note that use of different correlation functions does not affect in any significant manner either the work function or the exchange-correlation contribution to the surface energy, as obtained via the LDA, but do affect considerably the results for the total energy. This as explained earlier is because the component of the energy most sensitive to small variations in the effective potential is the kinetic energy, and its contribution to the total energy for high and medium densities is always significant.

APPENDIX

With the transformation $y = k_F x$, $k/k_F = q$, the slope parameter is $y_F = k_F x_F$, the metal surface is at $y_a = k_F a$, and the variable ζ is

$$\zeta = (y - q^2 y_F) y_F^{-1/3}. \qquad \text{(A1)}$$

We present below expressions for the phase shift, electronic density, metal surface position, surface dipole barrier, electrostatic potential, and the kinetic energy in terms of universal functions of the slope parameter y_F.

Phase shift

With the definition

$$\kappa(q, y_F) = y_F^{1/3} \frac{Ai(-q^2 y_F^{2/3})}{Ai'(-q^2 y_F^{2/3})}, \qquad \text{(A2)}$$

such that

$$\kappa(0) = y_F^{1/3} \frac{Ai(0)}{Ai'(0)} = -1.37172 y_F^{1/3}, \qquad \text{(A3)}$$

we have

$$\delta(q, y_F) = \cot^{-1}[1/q\kappa(q, y_F)]. \qquad \text{(A4)}$$

Electronic density

For $y \leqslant 0$

$$\frac{\rho_e(y)}{\bar{\rho}_e} = 1 - \tfrac{3}{2} \int_0^1 dq (1 - q^2) \cos 2[qy + \delta(q, y_F)]. \qquad \text{(A5)}$$

For $y \geqslant 0$

$$\frac{\rho_e(y)}{\bar{\rho}_e} = 3 \int_0^1 dq (1 - q^2) \sin^2 \delta(q, y_F) \times \frac{Ai^2((y - q^2 y_F) y_F^{-1/3})}{Ai^2(-q^2 y_F^{2/3})}. \qquad \text{(A6)}$$

The universal functions for the remaining properties were obtained by use of the following integral expressions.

$$\int Ai^2(\zeta)\, d\zeta = \zeta Ai^2(\zeta) - Ai'^2(\zeta), \qquad \text{(A7)}$$

$$\int \zeta Ai^2(\zeta)\, d\zeta = \tfrac{1}{3}[\zeta^2 Ai^2(\zeta) - \zeta Ai'^2(\zeta) + Ai(\zeta) Ai'(\zeta)], \qquad \text{(A8)}$$

$$\int Ai'^2(\zeta)\, d\zeta = \tfrac{1}{3}[-\zeta^2 Ai^2(\zeta) + \zeta Ai'^2(\zeta) + 2Ai(\zeta) Ai'(\zeta)]. \qquad \text{(A9)}$$

Metal surface position

Application of the charge neutrality condition of Eq. 18 leads to the expression

$$y_a = k_F a = -\frac{3\pi}{8} + \frac{2}{5} y_F - \tfrac{3}{2} \int_0^1 dq (1 - q^2) \frac{\sin 2\delta(q, y_F)}{2q}. \qquad \text{(A10)}$$

An alternate expression is obtained from the Sugiyama phase shift rule of Eq. 19:

$$y_a = -\frac{3\pi}{8} - 3 \int_0^1 dq\, q \delta(q, y_F). \qquad \text{(A11)}$$

Surface dipole barrier

$$\Delta\phi / k_F = (4/3\pi)[J(y_F) + K(y_F)], \qquad \text{(A12)}$$

where

$$J(y_F) = \frac{3}{4} \left(1 - \frac{2}{3} y_a^2 + \frac{\pi}{2} \kappa(0) + \int_0^1 dq \frac{(1 - q^2)\kappa^2}{1 + \kappa^2 q^2}\right), \qquad \text{(A13)}$$

and

$$K(y_F) = \frac{4}{35} y_F^2 - \frac{y_F}{2} \int_0^1 dq (1 - q^2) q \sin 2\delta(q, y_F). \qquad \text{(A14)}$$

Electrostatic potential

For $y \leqslant 0$,

$$\frac{V_{\mathrm{es}}(y)}{k_F} = \frac{4}{3\pi} \left(J(y_F) + \frac{3\pi}{8} y + \frac{y_a^2}{2} \Theta(y_a - y) + \tfrac{1}{2} y (2y_a - y) \Theta(y - y_a) + \frac{3}{4} \int_0^1 dq (1 - q^2) \frac{\cos 2\delta(q, y_F) \sin^2 qy}{q^2} + \frac{3}{8} \int_0^1 dq (1 - q^2) \frac{\sin 2\delta(q, y_F) \sin 2qy}{q^2}\right) \qquad \text{(A15)}$$

For $y \geqslant 0$

$$\frac{V_{\text{es}}(y)}{k_F} = \frac{\Delta\phi}{k_F} + \frac{2}{3\pi}(y-y_a)^2\Theta(y_a-y) - \frac{4y_F^{2/3}}{3\pi}\int_0^1 dq(1-q^2)\frac{\sin^2\delta(q,y_F)}{Ai^2(-q^2y_F^{2/3})} \times[2\zeta^2Ai^2(\zeta)-2\zeta Ai'^2(\zeta) - Ai(\zeta)Ai'(\zeta)]. \tag{A16}$$

Kinetic energy

$$\frac{E_k^{(1)}}{k_F^4} = (1/160\pi)\Theta, \tag{A17}$$

where

$$\Theta = 1 + \frac{80}{\pi}\left(\tfrac{3}{5}\int_0^1 dq\,q\delta(q,y_F) - \int_0^1 dq\,q^3\delta(q,y_F)\right), \tag{A18}$$

$$E_k^{(2)}/k_F^4 = (1/6\pi^2)[K(y_F)/y_F]. \tag{A19}$$

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[*] Supported in part by a grant from the City University of New York Faculty Research Program.

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