Metal surface energies in the infinite and step-potential approximations

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Jellium-metal surface energies for the infinite and finite step-potential barrier models have been obtained both by application of the Vannimenus-Budd theorem and by the determination of the individual components of the energy within the local exchange-correlation approximation. These two different methods for obtaining surface energies are then compared in light of their dependence on different physical properties. The barrier height in the step model is determined in each case either by the requirement of self-consistency of the surface dipole barrier or by application of the Budd-Vannimenus theorem, the metal surface position being fixed by the charge neutrality condition. An analytic expression for the derivative of the surface energy with respect to the Wigner-Seitz radius is also derived for the infinite-barrier model by use of the Vannimenus-Budd theorem. Finally a variational calculation of the surface energy within the local-density approximation is performed for the step model, the results closely approximating those of Lang and Kohn for medium and low densities.

I. INTRODUCTION

The surface energy of a metal, which is defined¹ as the energy required per unit area of new surface formed to split the crystal in two along a plane, is usually obtained by the determination of the individual components of the energy. These components are comprised of the kinetic, electrostatic, exchange, and correlation contributions. The original work^{2,3} on surface energies considered only the kinetic and electrostatic terms and that too in an approximate manner. More recently Lang and Kohn⁴ (LK), employing the densityfunctional formalism,^{5,6} have obtained surface energies including the contributions due to exchange and correlation in the so-called localdensity approximation (LDA). It has been shown⁷ that this approximation is meaningful provided it is made for the combined exchange and correlation contributions. The latter contributions to the surface energy have also been obtained^{8,9} in the random-phase approximation as applied to the infinite-potential-barrier model and although the results for the exchange and correlation terms taken separately are quite different from those of a local-density calculation, their sum is a fair approximation to the values obtained locally.⁷

A sum rule, whereby the surface energy of a jellium metal may be obtained without the determination of the individual components of the energy, has recently been derived by Vannimenus and Budd.¹⁰ The Vannimenus-Budd theorem (VBT) relates the derivative of the surface energy with respect to the Wigner-Seitz radius r_s in the bulk to the electrostatic potential inside the metal. The application of this sum rule thus simply requires the accurate determination of the total charge density inside the metal. In order to better understand this method for the determination of surface energies, it would therefore be of interest to compare the results of its application to a model potential of a metal surface to those obtained by the determination of the separate energy components. These calculations would also help in determining whether it is possible, by employing such model potentials with constraints, to obtain metal-surface properties comparable to those of other more complex formalisms.^{4,8}

In a recent paper¹¹ we attempted to answer this question by studying the step-potential model of a metal surface with respect to the surface dipole barrier and work function. The constraints employed there were the requirement of the selfconsistency of the surface dipole barrier and the satisfaction of a sum rule due to Budd and Vannimenus¹² relating the difference in electrostatic potential between that at the metal surface and that in the bulk to the energy per particle of a uniform electron gas. The results for the work function obtained¹¹ by application of the Budd-Vannimenus theorem¹² (BVT) proved generally superior to those obtained by the self-consistency condition and for $r_s = 3-6$ were within 0.28 eV of the results of LK.⁴

In Sec. IIA we obtained metal-surface energies in the infinite- and finite-potential-barrier models by application of the VBT. For the infinite-barrier model an analytic expression for the derivative of the surface energy with respect to the Wigner-Seitz radius has been obtained. The constraints on

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the metal-surface position being determined by the charge-neutrality condition.¹³ These results are then compared to those of a local exchangecorrelation calculation of the surface energy for these models presented in Sec. II B, where again the same constraints have been applied to define the effective potential. Model potentials, such as the step potential, parametrized by the barrier height and metal-surface position, also lend themselves naturally to variational^{14, 16, 17} calculations of the energy. The results of such a calculation in the LDA are also given¹⁴ in Sec. IIB together with the results of the application of the VBT for these variationally obtained values of the barrier height. Finally we discuss conclusions about these different methods of determining the surface energy and the limitations of the step and infinite-potential-barrier models with regard to each of these methods.

II. CALCULATION OF SURFACE ENERGIES

The step model of a metal surface for which the effective potential $V_{\rm eff}(\zeta)$ at the surface is $V_{\rm eff}(\zeta) = W\Theta(\zeta)$ [where W is the barrier height and $\Theta(\zeta)$ the step function] is defined fully in Ref. 11. We proceed here directly to the different calculations of the surface energies within this approximation. The results presented¹⁸ are in terms of the parameter $\beta = k_F/p$, where k_F is the Fermi momentum and $p^2 = 2W$. The permissible range of β in this model thus lies between zero and one.

A. Use of the Vannimenus-Budd theorem

According to the VBT,¹⁰ the derivative of the surface energy E_s with respect to the Wigner-Seitz radius r_s is given as

$$\frac{dE_s}{dr_s} = -\frac{9}{4\pi r_s^4} \int_{-\infty}^{-a} \left[V_{\rm es}(-\infty) - V_{\rm es}(\zeta) \right] d\zeta , \qquad (1)$$

where -a is the metal-surface position at which the jellium background begins and $V_{\rm es}(\zeta)$ the electrostatic potential. The surface energy may then be obtained by integration over r_s together with a suitable choice for the constant of integration.

We first consider the infinite-potential-barrier model for which $W \rightarrow \infty$ and the parameter $\beta = 0$. The total charge density and electrostatic potential are given as

$$\frac{\rho_T(z)}{k_F^3} = \frac{1}{3\pi^2} \left(1 + \frac{3\cos z}{z^2} - \frac{3\sin z}{z^3} - \Theta(-z-b) \right), \quad (2)$$

$$\frac{V_{\rm es}(z)}{k_F} = -\frac{1}{3\pi} \left[\frac{1}{2} (z^2 + b^2) - \frac{1}{2} (b+z)^2 \Theta(-z-b) - \frac{3}{2} \left(1 + \frac{\sin z}{z} + \int_0^z \operatorname{Si}(z') \, dz' \right) \right], \quad (3)$$

where

$$\operatorname{Si}(z) = \int_0^z \frac{\sin u}{u} du, \quad z = 2k_F \zeta, \quad b = \frac{3\pi}{4},$$

and where $V_{es}(z)$ is obtained by solution of Poisson's equation with the boundary conditions $V'_{es}(-\infty) = V_{es}(-\infty) = 0$. Performing the integration of Eq. (1) we obtain¹⁸

$$r_{s}^{4} \frac{dE_{s}}{dr_{s}} = -\frac{9}{4\pi} \times \frac{1}{4\pi} \left[-\frac{b^{3}}{3} - \frac{\pi}{2} + \frac{1}{2} (\sin b + b \cos b) + \left(1 + \frac{b^{2}}{2} \right) \operatorname{Si}(b) \right] = -0.009\,0304 \;.$$
(4)

Thus the surface energy E_s in erg/cm² in the infinite-potential-barrier model is obtained as

$$E_s = (4.689 \times 10^3) / r_s^3 + 59.990, \qquad (5)$$

where we fixed the constant of integration¹⁰ by matching E_s to the LK result for $r_s = 5$. The results for dE_s/dr_s and E_s are given in the left half of Table I together with the results $(dE_s/dr_s)_{LK-VB}$ and $(E_s)_{LK-VB}$ obtained¹⁰ by application of the VBT to the LK electrostatic potential. We observe that dE_s/dr_s is negative and that thus E_s is positive for all r_s in this model. On the other hand $(dE_s/$ $dr_s)_{\rm LK-VB}$ is negative for medium- and low-density metals but is positive and large for high-density metals, thus leading to positive surface energies for the former and negative energies for the latter. For $r_s \ge 3.0$ the results for E_s are fair approximations to those of $(E_s)_{LK-VB}$, the values being poorer for very-high-density metals. However, over the entire metallic range these results are vastly superior to those of a LDA calculation as discussed in Sec. II B. In addition the results for dE_s/dr_s also confirm another conclusion arrived at in Ref. 11; that this model is most valid for low-density metals only. It had been shown there that for this infinitepotential model the BVT is most closely approximated only in this range of r_s . In this case the shape of the two dE_s/dr_s curves are similar again only in the range $r_s \ge 4.3$ (see Fig. 2).

We next consider the application of the VBT to the finite-step model of a metal surface. In this model most properties of interest may be written¹¹ in terms of universal functions of the parameter β . The universal functions for the quantities $k_F a = g(\beta)$ and $\Delta \phi/k_F$, where $\Delta \phi$ is the surface dipole barrier, are given in Ref. 11. Expressions for the universal functions $\rho_T(z)/k_F^3$ and $V_{\rm es}(z)/k_F$ are given below:

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TABLE I.	Surface energies in erg/cm ²	the infinite-potential-barrier		
	Calculation via the	Calculation in		

		Calculation vi Vannimenus-Budo	Calculation in the local-density approximation			
rs	dE_s/dr_s	$(dE_s/dr_s)_{\rm LK-VB}^{a}$	Es	$(E_s)_{LK-VB}^{a}$	Es	$(E_s)_{LK}^{b}$
2.0	-879	4447	646	-980	4077	-1008
2.5	-360	755	360	49	1832	36
3.0	-174	79	234	197	964	199
3.5	- 94	-54	169	191	565	194
4.0	- 55	-71	133	157	359	158
4.5	- 34	-67	111	122	242	124
5.0	- 23	-34	97.5	97.5	170	98
5.5	- 15	-37	88	80	124	77
6.0	- 11	-33	82	62	94	60

^a These are the results of the application of the VBT to the Lang-Kohn electrostatic potentials. See Ref. 10.

^b See Ref. 4.

$$\frac{\rho_T(z)}{k_F^3} = \begin{cases} \frac{\beta^2}{\pi^2} \int_0^1 (1-q^2)q^2 \exp\left[-\beta^{-1}(1-\beta^2q^2)^{1/2}z\right] dq, & \text{for } z \ge 0\\ \frac{1}{\pi^2} \int_0^1 (1-q^2) \sin^2\left[\frac{1}{2}zq - \gamma(q)\right] dq - \frac{1}{3\pi^2}\Theta(-z-z_a), & \text{for } z \le 0 \end{cases}$$

and

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$$\frac{V_{es}(z)}{k_{F}} = \begin{cases} -\frac{\beta^{4}}{\pi} \int_{0}^{1} \frac{(1-q^{2})q^{2}}{1-\beta^{2}q^{2}} \exp\left[-\beta^{-1}(1-\beta^{2}q^{2})^{1/2}z\right] dq + \frac{\Delta\phi}{k_{F}}, & \text{for } z \ge 0\\ \frac{\beta^{2}}{\pi} \int_{0}^{1} (1-q^{2}) \left(\frac{1-2\beta^{2}q^{2}}{2\beta^{2}q^{2}}(1-\cos zq) - \frac{(1-\beta^{2}q^{2})^{1/2}}{\beta q}\sin zq\right) dq\\ + \frac{1}{\pi} \left[-\frac{1}{6}(z+z_{a})^{2}\Theta(z+z_{a}) + 1 + \frac{2}{3}\beta^{2} - \frac{1}{2}\beta\pi + \frac{1}{4}z\pi\right], & \text{for } z \le 0 \end{cases}$$

$$(7)$$

where $z = 2k_F\zeta$, $z_a = 2k_Fa$, $\sin\gamma(q) = \beta q$. Thus the integral of the electrostatic potential inside the metal is a universal function of β and we may write Eq. (1) as

$$r_{s}^{4} \frac{dE_{s}}{dr_{s}} = \frac{9}{4\pi} f(\beta) .$$
(8)

It has not been possible to obtain a closed-form analytic expression for $f(\beta)$ as was the case for the infinite-potential-barrier model. However, a numerically obtained plot of $f(\beta)$ is given in Fig. 1. Note that $f(\beta)$ is negative for all β and that therefore dE_s/dr_s will be negative for all r_s . The determination of dE_s/dr_s thus only requires an appropriate choice for the parameter β for each value of r_s . We fix the parameter β by the two separate criteria indicated in Ref. 11. First for each value of r_s , β is obtained by ensuring that the surface dipole barrier $\Delta \phi$ is obtained self-consistently. A plot of dE_s/dr_s for $2 \le r_s \le 6$, with this criterion for the choice of β , is shown as curve 2 of Fig. 2. The second method for the determination of β is to ensure that the electrostatic potential V_{es} either satisfies the BVT or approximates it as closely as possible.¹¹ The plot of dE_s/dr_s with this choice of β is shown as curve 3 of Fig. 2. The $(dE_s/dr_s)_{LK-VB}$ results are indicated by crosses on the graph.

model.

Comparison of the different curves for dE_s/dr_s indicates that curve 3 over the range over which it is nonzero more closely approximates the $(dE_s/dr_s)_{\rm LK-VB}$ results than does curve 1. We further note that application of the same BVT criterion also led to generally superior results for the surface dipole barrier. Thus these dE_s/dr_s plots reconfirm the importance of the BVT in such model calculations of metal-surface properties. Both dE_s/dr_s curves 2 and 3 for the step model, however, are better approximations to $(dE_s/dr_s)_{LK-VB}$ for small and medium densities than the infinitebarrier results (curve 1) which progressively become more negative over this range as r_s is decreased. The fact that neither curve 2 nor 3 becomes positive for small r_s is one of the limitations of the step model.

(6)





The surface energy E_s in each case is then obtained by integration over r_s with the constant of integration being chosen¹⁰ such that the E_s 's match those due to LK at $r_s = 5$. The results for E_s obtained from curves 2 and 3 are given in Table II. With the exception of $r_s = 3.5$ where the two sets of results are approximately the same, and $r_s = 3.0$ where the E_s obtained from curve 2 is superior since E_s is still rising, the results for the surface energy obtained by the BVT criteria are consistently better for all other densities. The fact that E_s obtained by this condition is constant for r_s = 2-3 and does not turn over and become negative for small r_s is again a consequence of the limita-



FIG. 2. Plots of the derivative of the surface energy E_s with respect to the Wigner-Seitz radius r_s vs r_s . Curve 1 is the result for the infinite-barrier model. Curves 2, 3, and 4 are the plots for the step-potential model as determined by the different criteria described in the text. The crosses represent the Lang-Kohn results as obtained by Vannimenus and Budd.

tion of this model with regard to this method for obtaining surface energies.

B. Local-density approximation

The determination of the surface energy via the VBT depends only on the electrostatic potential inside the metal and hence on the total charge den-

TABLE II. Surface energies E_s in erg/cm² for the finite step-potential model as obtained by application of the Vannimenus-Budd theorem (VBT) and the local-density approximation (LDA). For the set of results I, the barrier-height parameter β is determined by the self-consistency requirement of the surface dipole barrier; for the set II by the application of the BVT, and for the set III by variational minimization of the energy. The numbers in parentheses are the values of β for which the energy is a minimum.

	Calculation via the Vannimenus-Budd theorem				Calculation in the Local-density approximation				
rs	I	II	III	Lang-Kohn ^a	I	II	III ^b		Lang-Kohn ^c
2.0	287	148	137	-980	- 341	-390	(1.00)	-390	-1008
2.5	235	148	137	49	261	164	(1.00)	164	36
3.0	183	148	133	197	293	240	(0.980)	235	199
3.5	147	146	123	191	239	207	(0.946)	207	194
4.0	124	130	113	157	183	183	(0.904)	165	158
4.5	108	,111	104	122	141		(0.864)	130	124
5.0	98	98	98	98	109		(0.824)	102	98
5.5	90	88	92	80	85		(0.786)	81	77
6.0	85	82	88	62	67		(0.751)	65	60

^a See Ref. 10.

^b See Ref. 14.

^c See Ref. 4.

sity there. On the other hand, the individual components of the total surface energy within the localdensity approximation depend primarily upon the electronic charge density over all space.1 Components such as the kinetic energy have in addition an explicit dependence on the effective potential $V_{\rm eff}$ and the phase $\gamma(q)$ of the electronic wave function. Since the VBT is derived from the densityfunctional formalism, the results for the surface energy as obtained by LK are approximately the same as those obtained by application of the VBT to their self-consistent model.¹⁰ It is thus of interest to see how these two separate methods for the determination of the surface energy compare for the step model and how their dependence on different physical properties affect the final result.

The individual components of the total surface energy are comprised of the kinetic, electrostatic, exchange, and correlation contributions. As with the other properties, the kinetic energy E_k in the step model may be written in terms of a universal function of β which is given as¹⁻³

$$E_{k} = E_{k}^{(1)} - E_{k}^{(2)}, \qquad (9)$$

where

$$\frac{E_k^{(1)}}{k_F^4} = \frac{1}{2\pi^2} \int_0^1 \left(\frac{\pi}{4} - \gamma(q) - qg(\beta)\right) q(1-q^2) \, dq \,, \qquad (10)$$

$$\frac{E_k^{(1)}}{k_F^4} = \frac{1}{160\pi} \left[1 - \frac{4}{\pi} \left(1 - \frac{3}{\beta^2} + \frac{15}{8\beta^4} \right) \sin^{-1}\beta \right]$$

$$-\frac{1}{\beta\pi} \left(7 - \frac{15}{2\beta^2} \right) (1 - \beta^2)^{1/2} \right], \qquad (11)$$

$$E_{k}^{(2)} = \int_{-\infty}^{+\infty} \left(V_{\text{eff}} \left[\rho_{e}; \zeta \right] - V_{\text{eff}} \left[\rho_{e}; -\infty \right] \right) \rho_{e}(\zeta) \, d\zeta \,, \qquad (12)$$

$$\frac{E_{k^{2}}^{(2)}}{k_{f}^{4}} = \frac{1}{160\pi} \left[\frac{4}{\pi} \left(\frac{5}{\beta^{2}} - \frac{15}{4\beta^{4}} \right) \sin^{-1}\beta + \frac{1}{\beta\pi} \left(-10 + \frac{15}{\beta^{2}} \right) (1 - \beta^{2})^{1/2} \right].$$
 (13)

For the infinite-potential-barrier model ($\beta = 0$)

$$E_k/k_F^4 = E_k^{(1)}/k_F^4 = 1/160\pi; \quad E_k^{(2)} = 0,$$
 (14)

and for the other limit of the model for which the barrier height is at the Fermi level $(\beta = 1)$,

$$\frac{E_{k}^{(1)}}{k_{F}^{4}} = \frac{1}{160\pi} \times \frac{5}{4} ; \quad \frac{E_{k}^{(2)}}{k_{F}^{4}} = \frac{1}{160\pi} \times \frac{5}{2} ; \quad \frac{E_{k}}{k_{F}^{4}} = -\frac{1}{160\pi} \times \frac{5}{4} .$$
(15)

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

$$E_{\rm es} = \frac{1}{2} \int_{-\infty}^{+\infty} \rho_T(\zeta) V_{\rm es}(\zeta) d\zeta , \qquad (16)$$

and it can easily be seen that E_{es}/k_F^3 is a universal

function of β . Within the local-density approximation for which it has been shown⁷ that the exchange and correlation contributions must be taken together, the exchange and correlation energy is¹

$$E_{xc} = \int_{-\infty}^{+\infty} \left[\epsilon_{xc} (\rho_e(\zeta)) - \epsilon_{xc}(\overline{\rho}_e) \right] \rho_e(\zeta) \, d\zeta \,, \tag{17}$$

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. For ϵ_c the Wigner interpolation formula¹⁹ is employed.

The results of the three contributions to the total energy for the infinite-potential-barrier model are given in Table I. As with the results obtained via the VBT, the surface energies determined within the LDA are positive for all densities. The reason for this is that for this model the highly negative contribution $E_{k}^{(2)}$ to the kinetic energy vanishes so that E_{k} is positive for all densities. For medium and high densities the infinite barrier is too strongly confining, thus leading to very large values for the kinetic and hence the total energy. The results for the surface energy as obtained via the VBT, however, are superior to those obtained within the LDA for this model. A study of these results indicates that the LDA values can be as large as six times the value obtained via the VBT. This is a consequence of the fact that the LDA method for obtaining surface energies is particularly sensitive to the vanishing of the electronic density at the artificial barrier. As a result $E_{k}^{(2)}$ =0 and E_{es} and E_{xc} are considerably smaller than the corresponding values obtained by LK,⁴ these differences being particularly large for high and medium densities.

Thus the individual-component method for obtaining surface energies should lead to superior results for any more realistic model which permits a greater degree of electronic spill over. In Table II we present the results for the surface energy in the step-potential model, where, as in Sec. II A, the barrier-height parameter β is determined either by the requirement of self-consistency of $\Delta \phi$ (column I) or by the satisfaction of the BVT (column II). The latter results are given only for $r_s = 2-4$, since for $r_s > 4$ the BVT is most closely approximated by the infinite-potential-barrier model which as we have seen leads to guite unrealistic results for the surface energy as obtained by the individual-component method. These results, however, do appear in Table I. A study of the values for E_s of column I indicates their similarity to the results of LK, even becoming negative for $r_s = 2$. However, the model is too confining for all densities becoming progressively more confining for higher densities. For $r_s = 2-3.5$ the results of column II, however, are considerably superior to those of column I, being the same for $r_s = 4$. Although the model still too strongly reflects the electrons back into the metal, these results reaffirm the conclusion that better surface energies may be obtained by satisfying the condition set by the BVT.

It is also interesting to note that the results for E_{rc} are far superior to either those of E_{k} or E_{es} . This appears to indicate that the exchange-correlation energy as obtained in the LDA is considerably less sensitive to the choice of effective potential than are the kinetic- and electrostatic-energy terms. For low densities this has added significance since E_{xc} is the primary contributor to the total energy. The reason for the above accuracy may be that in addition to the fact that the errors in the exchange and correlation contributions cancel, E_{rc} in the LDA depends explicitly only on the electronic density, and any reasonable effective potential leads to fairly accurate electronic densities. This is further borne out by the fact that for $r_s \ge 3.0$, densities for which over 68% of the contribution to the surface dipole barrier is due to electronic charge outside the metal, the results for $\Delta \phi$ in the step model¹¹ are within 0.28 eV of those due to LK provided the BVT is satisfied.

For the variational calculation it is assumed that the total energy of a metal is the sum of the bulk- and surface-energy contributions. Furthermore, since the Friedel oscillations of the electronic charge density essentially vanish within a few Fermi wavelengths of the metal surface, it may also be assumed that it is only those electrons near the surface which are aware of the presence of the effective potential at the metal surface. Thus it is only the surface energy term that is a function of any parameters used to describe the effective potential. Variational minimization of the total energy thus involves minimization of the surface energy with respect to these parameters. In the step-potential model it is the barrier-height parameter β with respect to which the surface energy has to be minimized. The results of a variational calculation¹⁴ within the LDA for the step model are given in column III of Table II. For $r_s = 2.5-6$ there is an energy minimum at the values of β quoted in parentheses. For $r_s < 2.5$ there is no such energy minimum. The minimum energy for such high densities is thus obtained in the $\beta = 1$ limit of the model.

We note that the variational method leads to the best set of results for low and medium densities. For $r_s = 3.5-6$ the energies are within 8.2% of those due to LK, indicating thereby that the approximation of separating the total energy into a

surface and bulk component is physically meaningful. Furthermore, for $r_s \ge 3.5$ the derivative of the surface energy as obtained from these results for E_s also closely approximates the $(dE_s/dr_s)_{\rm LK-VB}$ results. However, since the corresponding values of β are larger than either those obtained by the self-consistency or BVT condition, the results for the derivative (curve 4 of Fig. 2) as determined by the VBT from the universal curve of Fig. 1 and hence the energy (column III) are the least accurate. For high densities, the variational results are the same as those obtained by application of the BVT, and this model cannot therefore lead to results for $r_s = 2.0$ and 2.5 which are superior to those given in column II.

Since we have employed the variational principle for the energy, our results for the surface energy constitute an upper bound to this property. Although the LK results for the surface energy are lower, they do not constitute an upper bound since they are obtained by solution of the self-consistent equations of Kohn and Sham⁶ and not from the exact density-functional formalism of Hohenberg, Kohn, and Sham^{5,6} for which the energy is a minimum. However, properties other than the energy, such as the surface dipole barrier, determined by employing wave functions obtained by energy minimization will be correct only to the same order as that of the wave function and in general will not be as accurate as the energy.^{11,20} One therefore needs to employ variational methods whereby properties other than the energy are themselves obtained correct to second order. Recently variational methods^{20,21} for obtaining singleparticle expectation values of Hermitian operators to second order have been developed and are presently being employed to determine the electronic charge density at metal surfaces.

The results of the various calculations indicate that the surface energy as obtained in the LDA is particularly sensitive to the choice of the effective potential and hence to the electronic density near the metal surface. This is borne out in particular by the results of the infinite- and finite-potentialbarrier models. The fact that the results of the LDA calculation for the more realistic finite-barrier model are superior to those obtained by application of the VBT is again a consequence of the dependence of the individual components of the energy on the electronic density. Even though, for example, in the exchange term one considers the difference between the local and bulk values of the exchange energy, the primary contribution to E_{xc} is near the metal surface where this difference is largest. Similarly, the primary contribution to the electrostatic-energy term is due to the electronic density outside the metal and the electrostatic potential which arises from it. On the other hand use of the VBT depends only on the electrostatic potential inside the metal. This in turn depends on the total charge density there, which is obtained by subtracting the positive-charge background from the electronic density. The percentage errors of the total density are thus a magnification of the percentage errors of the electronic density. Thus the derivative of the surface energy with respect to r_s is a property which is even more sensitive to the choice of the effective potential. The primary advantage of the VBT is that one does not have to determine the individual components of the energy, but on the other hand it proves to be a far more stringent requirement to satisfy. The theorem would be particularly powerful if accurate densities could be obtained without making any approximations with regard to exchange and correlation. For the step model, however, dE_s/dr_s may be determined directly from the universal function $f(\beta)$ of Fig. 1, once a criterion for the choice of the parameter is developed. Finally we note that these calculations reaffirm the importance of the BVT since consistently good results are obtained by its application irrespective of the method being employed to obtain the density.

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- ¹N. D. Lang, in Solid State Physics, Advances in Research and Applications, edited by H. Ehrenreich,
 F. Seitz, and D. Turnbull (Academic, New York, 1973),
 Vol. 28.
- ²H. B. Huntington, Phys. Rev. <u>81</u>, 1035 (1951).
- ³R. Stratton, Philos. Mag. <u>44</u>, 1236 (1953).
- ⁴N. D. Lang and W. Kohn, Phys. Rev. B <u>1</u>, 4555 (1970); <u>3</u>, 1215 (1971). The self-consistency procedure has been numerically refined by Lang and the improved results quoted in the text.
- ⁵P. Hohenberg and W. Kohn, Phys. Rev. B <u>136</u>, 864 (1964).
- ⁶W. Kohn and L. J. Sham, Phys. Rev. <u>140</u>, A1133 (1965).
- ⁷N. D. Lang and L. J. Sham, Solid State Commun. <u>17</u>, 581 (1975).
- ⁸J. Harris and R. O. Jones, J. Phys. F <u>4</u>, 1170 (1974).
- ⁹E. Wikborg and J. E. Inglesfield, Solid State Commun. 16, 335 (1975).
- ¹⁰J. Vannimenus and H. F. Budd, Solid State Commun. <u>15</u>, 1739 (1974).
- ¹¹V. Sahni, J. B. Krieger, and J. Gruenebaum, Phys. Rev. B 12, 3503 (1975).

- ¹²H. F. Budd and J. Vannimenus, Phys. Rev. Lett. <u>31</u>, 1218 (1973); 31, 1430(E) (1973).
- ¹³J. Bardeen, Phys. Rev. <u>49</u>, 653 (1936).
- ¹⁴J. H. Rose and H. B. Shore, Solid State Commun. <u>17</u>, 327 (1975). The results of these authors for the surface energy for both the infinite and step models have been obtained by employing densities determined by approximate numerical solution of the Schrödinger equation (Ref. 15). The values quoted in Tables I and II of the text, however, employ the analytic expressions for E_k and k_Fa and the exact densities for the determination of E_{es} and E_{xc} .
- ¹⁵H. B. Shore (private communication).
- ¹⁶G. Paasch and M. Hietschold, Phys. Status Solidi B <u>67</u>, 743 (1975).
- ¹⁷G. D. Mahan, Phys. Rev. B <u>12</u>, 5585 (1975).
- ¹⁸Atomic units are used: $|e| = \overline{h} = m = 1$. The unit of energy is 27.21 eV.
- ¹⁹D. Pines, *Elementary Excitations in Solids* (Benjamin, New York, 1963), p. 94.
- ²⁰J. B. Krieger and V. Sahni, Phys. Rev. A <u>6</u>, 919 (1972).
- ²¹V. Sahni and J. B. Krieger, Phys. Rev. A 8, 65 (1973).