Exchange-correlation energy of a metallic surface: Wave-vector analysis*

David C. Langreth

Nordita, Copenhagen, Denmark
and Rutgers University,[†] New Brunswick, New Jersey 08903

John P. Perdew

Rutgers University, New Brunswick, New Jersey 08903
(Received 12 November 1976)

The exchange-correlation energy of a jellium metal surface is analyzed in terms of the wavelength of the fluctuations that contribute to it, using a three-dimensional scheme different from that used by other authors. It is shown that with this scheme there exists an exact limiting form at long wavelengths which includes all many-body correlations and which is independent of the surface density profile. The local-density approximation is formulated as a function of wavelength, and it is shown to be exact at short wavelength. The interpolation scheme between these limits, which was discussed previously, is formulated and checked more completely and used to calculate surface energies.

I. INTRODUCTION

The metal surface, aside from its practical importance, is an interesting example of an extremely inhomogeneous electron system. Its simplest ground-state property is the surface energy (energy required to create a unit area of new surface).

The first calculation of metal surface energies which attempted to treat exchange and correlation effects realistically was performed by Lang and Kohn,[1] who divided the surface energy into two pieces. The first piece is that associated with the self-consistent jellium model, in which the ions are replaced by a semi-infinite uniform positive background; this piece is further subdivided into kinetic, electrostatic, and exchange-correlation energy contributions. The second piece includes the classical cleavage energy of a neutralized lattice and the ion pseudopotential contribution. The results of Lang and Kohn are in quantitative or semiquantitative agreement with measured surface tensions for many simple metals.

The importance of exchange and correlation is evident in the work of Lang and Kohn, since the other contributions to the surface energy, while they may be individually large, show some tendency to cancel one another, leaving the total surface energy roughly comparable in value to, or smaller than, the exchange-correlation contribution alone.

Lang and Kohn treat exchange and correlation in the local-density approximation (LDA)

$$E_{xc} = \int d^3x\, n(\vec{x}) \epsilon_{xc}(n(\vec{x})) \ , \qquad (1.1)$$

where $n(\vec{x})$ is the electron density and $\epsilon_{xc}(n)$ is the exchange-correlation energy per electron of a homogeneous electron gas of density n. The LDA is presumably valid when the spatial variation of the density is slow compared with both the Fermi wavelength and the screening length.[2] This criterion is not satisfied for a metal surface, and consequently the validity of the Lang-Kohn calculation has been open to challenge.

A very different approach to the surface energy has been taken by Schmit and Lucas[3] and by Craig.[4] Although their approach is oversimplified, and has been highly criticized,[5] it clearly points to a contribution from a shift in plasmon zero-point energies which can be only poorly imitated by a local approximation. Their work provided the impetus for a number of contributions[6-14] which in one way or another either treated the question of how good the local approximation for exchange and correlation was, or of the relative contributions[15] of plasmon modes versus single-particle modes to the surface energy. Instead of trying to make a division between plasmon and particle-hole modes, we have found it more fruitful to ask what are the relative contributions of *long* versus *short* wavelength fluctuations. Schmit and Lucas clearly point out that long-wavelength fluctuations may be important. These are not included accurately in the local density approximation. The questions which we set out to investigate were therefore (i) how good the local approximation was and (ii) could it be improved by a more accurate inclusion of the long-wavelength fluctuations? A summary of our results has been presented earlier.[13]

Here we derive in more detail the wave-vector decomposition of the exchange-correlation energy of an inhomogeneous system. This is different from the two-dimensional decomposition suggested by Schmit and Lucas and followed by other authors, since at small wave vector we show that there is an exact limiting form which includes all many-body effects and which is independent of the surface-density profile. We next formulate the local-density approximation as a function of wave vector, and show that it makes an infinite error at small wave vector, as compared with our exact form. At large wave vector, on the other hand, we show that this local approximation becomes exact. Thus we propose an interpolation scheme between small and large wave-vector. This scheme is tested and verified for the soluble infinite barrier model in random-phase approximation (RPA), and then applied to self-consistently calculated density profiles. For these it is found that the local-density approximation is accurate to better than 10%, for the exchange-correlation energy.[16]

II. "WAVE VECTOR" DECOMPOSITION OF EXCHANGE-CORRELATION ENERGY

Many years ago Nozières and Pines[17] showed it useful in the calculation of the energy of an infinite (bulk) electron gas to decompose the correlation energy into a sum over fluctuations of different wave vectors, and to use one approximation for small wave vector and another for large. Here we do the same thing for the surface energy. There are several differences, however, which we discuss below.

First, in the bulk the exchange energy can be easily calculated exactly and is considerably larger in magnitude than the correlation energy. This leads one to consider the correlation energy alone. On the other hand the surface contribution to the correlation and exchange energies are each of the same order[9] and neither can be calculated exactly. Therefore it is unprofitable (and in fact turns out to be even counterproductive) to effect an artificial separation of the two. Therefore we consider mainly the sum of the two δE_{xc} which we define precisely below.

The second difference is that in the bulk the wave vector $\vec{K}$ of a fluctuation, as it corresponds to its momentum, is a good quantum number. Thus one in this case has a natural and unambiguous way in which to make the desired decomposition as a sum of the energies associated with the good quantum number $\vec{K}$. In the surface case, there is at least for jellium an analogous good quantum number in

the wave vector $\vec{k}$ parallel to the surface. It is tempting to follow the implicit suggestion of the original work of Schmit and Lucas[3] which has been used profitably for example by Griffin, Kranz and Harris,[11] Wikborg and Inglesfield,[9] and to decompose E_{xc} into a sum of such excitations. Such a decomposition we found not to be useful for some of our purposes, because as shown later such a decomposition depends in an unknown (i.e., difficult to calculate) way on the details of the surface-density profile. We therefore chose to return to a three-dimensional wave vector $\vec{K}$. Since the component Q of $\vec{K}$ perpendicular to the surface does not correspond to any conserved quantity, it is not even obvious a priori how to define this wave-vector decomposition.

The Hamiltonian H we divide into two pieces $H_k + H_i$, where H_k is the N-particle kinetic-energy operator and H_i is everything else. Since we anticipate making the usual type of coupling-constant integration, we let H_i be a function of a dimensionless coupling constant λ which varies between 0 and 1 with $\lambda = 1$ corresponding to the real physical system:

$$H_i = \tfrac{1}{2} \int d^3x \int d^3x' \, V_\lambda(\vec{x} - \vec{x}')n(\vec{x})[n(\vec{x}') - \delta(\vec{x} - \vec{x}')]$$

$$+ \int d^3x \, v_\lambda(\vec{x})n(\vec{x}) . \tag{2.1}$$

Here $n(\vec{x})$ is the number density operator for the electrons. V_λ is the interelectronic interaction which is taken to be linear in λ: $\lambda e^2/|\vec{x} - \vec{x}'|$. The δ-function term in (2.1) is an (infinite) self-interaction which depends only on the total number of particles N and hence does not contribute to the surface energy. For $\lambda = 1$, $v_\lambda(\vec{x})$ is the potential due to the uniform positive background filling the region of space occupied by the sample. Just as in the bulk case, we chose the λ dependence of v such that the coupling constant integral can be done at constant electronic density; thus $v_\lambda(\vec{x})$ will depend linearly on λ for $\vec{x}$ in the interior of the sample far from the surface, but near the surface this dependence is unknown a priori. Harris and Jones[8] have proposed a somewhat different scheme for the coupling-constant integration, where v_λ is taken to be a linear function of λ everywhere. For our purposes their scheme has not proved useful, except for the infinite-barrier model where the schemes coincide. The present method, which we used in Ref. 13, has also been used by Gunnarsson and Lundqvist.[18] We have that, letting E_λ be the ground-state energy of H for a given λ and $\langle \cdots \rangle_\lambda$ be the ground-state expectation value (for a given λ)

$$E_1 - E_0 = \int_0^1 d\lambda \frac{dE_\lambda}{d\lambda} = \int_0^1 d\lambda \left\langle \frac{\partial H_i}{\partial \lambda} \right\rangle_\lambda$$

$$= \int_0^1 \frac{d\lambda}{2\lambda} \int d^3x \int d^3x' \, \lambda V_1(\tilde{x} - \tilde{x}') \langle n(\tilde{x})[n(\tilde{x}') - \delta(\tilde{x} - \tilde{x}')]\rangle_\lambda + \int_0^1 d\lambda \frac{\partial}{\partial \lambda} \int d^3x \, [v_\lambda(\tilde{x}) \langle n(\tilde{x})\rangle_\lambda],$$

$$(2.2)$$

where we have used the independence of $\langle n(\tilde{x})\rangle_\lambda$ on λ to pull the λ derivative outside the brackets in the last line. We now make the following definitions (of T, E_{coul}, and E_{xc}, respectively):

$$E_0 = T + \int d^3x \, v_0(\tilde{x})\langle n(\tilde{x})\rangle, \qquad (2.3)$$

$$E_{\text{coul}} = \tfrac{1}{2} \int d^3x \int d^3x' \, V_1(\tilde{x} - \tilde{x}')\langle n(\tilde{x})\rangle\langle n(\tilde{x}')\rangle$$

$$+ \int d^3x \, v_1(\tilde{x})\langle n(\tilde{x})\rangle, \qquad (2.4)$$

and

$$E \equiv E_1 = T + E_{\text{coul}} + E_{xc}, \qquad (2.5)$$

where the subscripts "1" and "0" imply $\lambda = 1$ and $\lambda = 0$, respectively. Note that T is not the expectation value of the kinetic-energy operator but rather what the kinetic energy would be in a non-interacting system with the same electronic density $n(\tilde{x})$. The definition (2.5) of E_{xc} thus corresponds to precisely that which is customarily used in density functional theory. Upon performing the λ integration and using (2.3)–(2.5) one gets

$$E_{xc} = \tfrac{1}{2} \int_0^1 \frac{d\lambda}{\lambda} \int d^3x \int d^3x' \, V_\lambda(\tilde{x} - \tilde{x}')$$

$$\times [N S_\lambda(\tilde{x}, \tilde{x}') - \langle n(\tilde{x})\rangle\delta(\tilde{x} - \tilde{x}')], \qquad (2.6)$$

where

$$N S_\lambda(\tilde{x}, \tilde{x}') = \langle [n(\tilde{x}) - \langle n(\tilde{x})\rangle]$$

$$\times [n(\tilde{x}') - \langle n(\tilde{x}')\rangle]\rangle_\lambda. \qquad (2.7)$$

The factor N, the total number of electrons, is included to make S coincide with the usual definitions.

We now introduce the wave vector $\vec{K}$ which is basic to our decomposition and write

$$E_{xc} = \int \frac{d^3K}{(2\pi)^3} \frac{1}{2} \int_0^1 \frac{d\lambda}{\lambda} \left(\frac{4\pi e^2\lambda}{K^2} \right) N[S_\lambda(\vec{K}) - 1], \qquad (2.8)$$

where

$$S_\lambda(\vec{K}, \vec{K}') = \int d^3x \int d^3x' e^{-i\vec{K}\cdot\tilde{x} + i\vec{K}'\cdot\tilde{x}'} S_\lambda(\tilde{x}, \tilde{x}')$$

$$(2.9)$$

and $S_\lambda(\vec{K}) \equiv S_\lambda(\vec{K}, \vec{K})$.

Note that Eqs. (2.6) and (2.9) have both bulk and surface contributions in the limit of a large sample, and, for example, we may write

$$N S_\lambda(\vec{K}) = N S_\lambda^B(\vec{K}) + N\delta S_\lambda(\vec{K}), \qquad (2.10)$$

where $N S_\lambda^B(\vec{K})$ is of order of the volume of our finite sample and is equal to N times the structure factor for an electron density equal to that of the interior. The quantity $N\delta S_\lambda(K)$ is the surface correction to $NS_\lambda(K)$ and is proportional to the surface area of our sample. In writing (2.10) and everywhere else in this paper we assume that $K \gg 1/L$, where L is a length characterizing a linear dimension of the sample or the curvature of any macroscopic part of it. We use (2.10) to rewrite the total and surface components of E_{xc}, respectively as

$$E_{xc} = \int \frac{d^3K}{(2\pi)^3} E_{xc}(\vec{K}),$$

$$\delta E_{xc} = \int \frac{d^3K}{(2\pi)^3} \delta E_{xc}(\vec{K}), \qquad (2.11)$$

$$E_{xc}(\vec{K}) = \tfrac{1}{2} \int_0^1 \frac{d\lambda}{\lambda} \frac{4\pi e^2\lambda}{K^2} N[S_\lambda(\vec{K}) - 1],$$

$$\delta E_{xc}(\vec{K}) \equiv \tfrac{1}{2} \int_0^1 \frac{d\lambda}{\lambda} \frac{4\pi e^2\lambda}{K^2} N\delta S_\lambda(\vec{K}), \qquad (2.12)$$

where δE_{xc} is the surface contribution to the exchange-correlation energy. Equation (2.12) serves as a *definition* of $E_{xc}(\vec{K})$ and $\delta E_{xc}(\vec{K})$ and hence of the wavelength decomposition to be used extensively in this paper (as it was in Ref. 13). Note that $\delta E_{xc}(\vec{K})$ depends not only on $K \equiv |\vec{K}|$ but also on the angle θ between $\vec{K}$ and the surface normal. In order to obtain a one-parameter measure of δE_{xc} as a function of fluctuation wave vector, it is convenient to take a spherical average

$$\delta E_{xc}(K) \equiv \tfrac{1}{2} \int_0^\pi d\theta \sin\theta \, \delta E_{xc}(\vec{K}). \qquad (2.13)$$

Note that this is a definition and not an approximation, as the left-hand side of (2.13) can still be used (exactly) in place of $\delta E_{xc}(\vec{K})$ in the right-hand side of (2.11). The choice of a spherical average (2.13) is arbitrary, but convenient because the remaining (one dimensional) integral in (2.11) has

a simple weight factor $4\pi K^2/(2\pi)^3$. We could equally well have chosen to average $\delta E_{xc}(\vec{K})$ over some other closed surface of characteristic linear dimension K (rather than a sphere), in which case (2.13) would be modified by a dimensionless geometrical factor (of order unity) which would cancel out in the final result (2.11).

We stress two points. First neither K nor $\vec{K}$ represents the quantum number of a conserved quantity, so that (2.11) does not represent the sum of zero-point energies of modes, although on the average our intuitive notions concerning "long wavelength" versus "short wavelength" should still hold. Second (2.11) is not the usual wave-vector decomposition previously applied to the surface-energy problem by Schmit and Lucas,[3] Harris and Jones,[8] Griffin, Kranz, and Harris,[11] Wikborg and Inglesfield,[9] and others. The latter involves only the two-dimensional wave vector $\vec{k}$ parallel to the surface, which is a conserved quantity. The relationship between this latter decomposition and (2.11) is, letting $\vec{K} = (\vec{k}, Q)$,

$$\delta E_{xc} = \int \frac{d^2k}{(2\pi)^2}\, \delta \bar{E}_{xc}(k) , \qquad (2.14)$$

where

$$\delta \bar{E}_{xc}(k) = \int_{-\infty}^{\infty} \frac{dQ}{2\pi}\, \delta E_{xc}(\vec{K}) . \qquad (2.15)$$

In Sec. III we prove that the small K (but as always $K \gg L^{-1}$) limit of $\delta E_{xc}(K)$ is dominated by the change in zero-point energies of plasmons, and is independent of the details of the surface. On the other hand we show that $\delta \bar{E}_{xc}(k)$ is not dominated by plasmons even as $k \to 0$ and is sensitive to surface details (Appendix C).

We conclude this section by noting that the popular local-density approximation (LDA) to E_{xc} may be decomposed into wave-vector components in the same way. For example, in the LDA, Eq. (2.8) becomes

$$E_{xc} = \int \frac{d^3K}{(2\pi)^3} \int d^3x\, \tfrac{1}{2} \int_0^1 \frac{d\lambda}{\lambda} \frac{4\pi e^2 \lambda}{K^2}$$

$$\times n(\vec{x})[S_\lambda^B(K;\, n(\vec{x})) - 1], \qquad (2.16)$$

where $S_\lambda^B(K;\, n(\vec{x}))$ is the same functional form as the bulk $S_\lambda^B(K)$ at the uniform electron density n, but with n replaced by the actual density profile $n(\vec{x})$. [We use the same symbol for the density operator and its expectation value, except where this could lead to confusion, as in Eq. (2.7). Here $n(\vec{x}) \equiv \langle n(\vec{x}) \rangle$.] Since we need only the surface contribution, we have for the LDA to $\delta E_{xc}(K)$

$$\delta E_{xc}(K) = \int d^3x\, \tfrac{1}{2} \int_0^1 \frac{d\lambda}{\lambda} \frac{4\pi e^2 \lambda}{K^2}$$

$$\times [n(\vec{x})\, S_\lambda^B(K;\, n(\vec{x})) - n_0(\vec{x}) S_\lambda^B(K;\, n_0(\vec{x}))] , \qquad (2.17)$$

where $|e|n_0(\vec{x})$ is the charge density of the uniform (where it is nonzero) jellium background. We note that the approximation (2.17) to δE_{xc} is already independent of the direction of $\vec{K}$ without spherical averaging as in (2.13). In the same manner as Eqs. (2.14) and (2.15) one can also define the LDA to $\delta \bar{E}_{xc}(k)$.

III. LONG-WAVELENGTH LIMIT

In this section[19] we derive the exact form of $\delta E_{xc}(K)$ at small K that was used in Ref. 13. We shall show that our expression is independent of the details of the surface, and is valid with all many-body corrections included. In fact with no further difficulty we derive limiting expressions for the dynamic susceptibility (density response) and form factor which may be useful in other contexts.

We show that in the limit of small three-dimensional wave vector K, the component of the exchange-correlation energy $\delta E_{xc}(K)$ is dominated by plasmon zero-point energies. It is given by an expression [Eq. (3.34)] reminiscent of that obtained by Schmit and Lucas[3] and Craig,[4] whose work played an important role in motivating our early thinking. Nevertheless, the expression given by these authors involves the two-dimensional wave vector k, and turns out not to be correct at small k, as we show, because the limit of small two-dimensional k is not dominated by shifts in the zero-point energies of plasmons.

We define the susceptibility in the usual way, as the linear density response $\delta n(\vec{x})$ to an external potential $\phi_0(\vec{x}')$:

$$\delta n(\vec{x}) = \int d^3x'\, \chi(\vec{x}, \vec{x}', \omega)\phi_0(\vec{x}'), \qquad (3.1)$$

where we assume that ϕ_0 and hence δn are turned on to adiabatically from $t = -\infty$, and are proportional to $e^{-i\omega t}$ at finite times. [In this section we for the most part suppress the coupling-constant (λ) dependence of all quantities.] We define the dynamic form factor $S(\vec{x}, \vec{x}', \omega)$ in the usual way as

$$S(\vec{x}, \vec{x}', \omega) = \int_{-\infty}^{\infty} \frac{dt}{2\pi}\, e^{i\omega t} \langle [n(\vec{x}, t) - \langle n(\vec{x}, 0)\rangle]$$

$$\times [n(\vec{x}', 0) - \langle n(\vec{x}', 0)\rangle] \rangle, \qquad (3.2)$$

where $n(\vec{x}, t)$ is the Heisenberg density operator [cf. Eq. (2.7)]. In terms of this we easily obtain the static form factor

$$NS(\tilde{x}, \tilde{x}') = \int_{-\infty}^{\infty} d\omega \, S(\tilde{x}, \tilde{x}', \omega) . \tag{3.3}$$

Finally, after calculating χ, we obtain S from the zero temperature limit of the appropriate fluctuation-dissipation theorem

$$S(\tilde{x}, \tilde{x}', \omega) = -(1/\pi) \, \text{Im} \, \chi(\tilde{x}, \tilde{x}', \omega)\Theta(\omega) , \tag{3.4}$$

where $\Theta(\omega) = 1$ for $\omega > 0$ and zero otherwise.

For compactness we adopt a matrix notation for three-dimensional space integrals so that for example Eq. (3.1) becomes $\delta n = \chi \phi_0$. Upon defining ϕ as the *total* potential (due to external and induced charges)

$$\phi = \phi^0 + V\delta n, \tag{3.5}$$

where V is (the matrix representation of) the Coulomb interaction, we let χ^0 be the density response to this potential

$$\delta n = \chi^0 \phi . \tag{3.6}$$

Note well that χ^0 is not the susceptibility of the noninteracting system (except in the random-phase approximation) and is defined diagrammatically in Fig. 1. Equations (3.1), (3.5), and (3.6) imply that

$$\chi = \chi^0 + \chi^0 V\chi , \tag{3.7}$$

and it is this latter equation whose solution we shall investigate.

We now introduce the cosine transform representation mentioned in Appendix A for variation perpendicular to the surface. For this purpose we introduce an artificial infinite barrier at the origin (in the y-z plane) to rigorously confine the electrons to the right-hand half space. Since we let the jellium background begin at a point $x = x_0$, where x_0 is larger than the surface healing length, the error in this artificial procedure can be made exponentially small. The double cosine transform of the Coulomb interaction

$$V_{qq'} \equiv \int_0^{L/2} dx \int_0^{L/2} dx' \, C_q(x)C_{q'}(x') \frac{2\pi e^2}{k} e^{-k|x-x'|} \tag{3.8}$$

can be written

$$V_{qq'} = \alpha v_q \underline{1}_{qq'} - \alpha v_q v_{q'} , \tag{3.9}$$

where

$$\alpha = 2\pi e^2/k \tag{3.10a}$$

and

$$v_q = 2k/(k^2 + q^2) , \tag{3.10b}$$

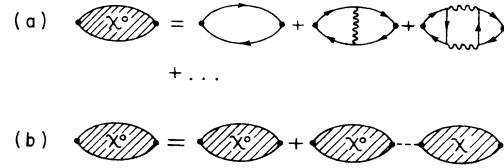where $\tilde{k}$ is the Fourier-transform variable parallel to the surface and is common to all the factors

FIG. 1. (a) Typical diagrams for χ^0. Here the solid line represents the full electron propagator and the wavy line is the fully screened Coulomb interaction V/ϵ $= V/(1 - V\chi^0)$. (b) The integral equation for χ in terms of χ^0. The dashed line is the bare Coulomb interaction V.

in (3.9). The quantity $C_q(x)$ is equal (as in Appendix A) to 2 $\cos qx$. Note that the length of the jellium background is $\frac{1}{2}L - x_0$. Finally the quantity $\underline{1}_{qq'}$ is the unit matrix in our cosine transform space as defined in Appendix A.

The second term has 2 factors of v_q which is singular for small k and q, and this suggests treating them differently. Hence we let $V = V^{(1)} + V^{(2)}$, where

$$V_{qq'}^{(1)} = \alpha v_q \underline{1}_{qq'}, \quad V_{qq'}^{(2)} = -\alpha v_q v_{q'} . \tag{3.11}$$

It is now a matter only of algebraic manipulation (see Appendix B) to show that $\chi_{qq'}$ the double cosine transform of χ is given by

$$\chi_{qq'} = \bar{\chi}_{qq'} - \sum_{\bar{q}\,\bar{q}'} (\bar{\chi}_{q\bar{q}}\, v_{\bar{q}}) \frac{\alpha}{D} (v_{\bar{q}'} \bar{\chi}_{\bar{q}'q'}) , \tag{3.12}$$

where

$$D = 1 + \alpha \sum_{qq'} v_q v_{q'} \bar{\chi}_{qq'} \tag{3.13}$$

and where the summation goes over non-negative q as defined in Appendix A, and which for most purposes can be thought of as $(2\pi)^{-1} \int_0^\infty dq$. The quantity $\bar{\chi}_{qq'}$ must be obtained by solving the integral equation

$$\bar{\chi}_{qq'} = \chi_{qq'}^0 + \sum_{\bar{q}} \chi_{q\bar{q}}^0 \, V_{\bar{q}} \bar{\chi}_{\bar{q}q'} , \tag{3.14}$$

where $\chi_{qq'}^0$ is the double cosine transform of χ^0 and where

$$V_q = 4\pi e^2/(q^2 + k^2) = \alpha v_q$$

is simply the three-dimensional exponential Fourier transform of the Coulomb interaction V. Note that the quantities $\chi_{qq'}^0$, $\bar{\chi}_{qq'}$ and $\chi_{qq'}$ are also functions of $\tilde{k}$, the wave vector parallel to the surface, and the frequency ω.

It is now convenient to separate (3.14) into "bulk" and "surface" terms. For this purpose we introduce the bulk dielectric function $\epsilon(\tilde{K}, \omega)$ of a uniform electron gas with the same constant

electron density as our bounded gas has in its interior far from the surface. We note the following definitions:

$$\epsilon(\vec{K}, \omega) \equiv \epsilon((k^2 + q^2)^{1/2}, \omega) \equiv \epsilon_q \equiv 1 - V_q \chi_q^{0B} , \qquad (3.15)$$

hence defining the *bulk* density response χ_q^{0B} to a self-consistent potential with wave vector $\vec{K} = (q, \vec{k})$. Hence we let

$$\chi_{qq'}^0 = \chi_q^{0B} \underline{1}_{qq'} + \psi_{qq'}^0 , \qquad (3.16)$$

$$\bar{\chi}_{qq'} = (\chi_q^{0B}/\epsilon_q) \underline{1}_{qq'} + \psi_{qq'}/\epsilon_q \epsilon_{q'} , \qquad (3.17)$$

thus defining the deviation functions $\psi_{qq'}^0$ and $\psi_{qq'}$. Then Eq. (3.14) becomes

$$\psi_{qq'} = \psi_{qq'}^0 + \sum_{\bar{q}} \psi_{q\bar{q}}^0 \frac{V_{\bar{q}}}{\epsilon_{\bar{q}}} \psi_{\bar{q}q'} . \qquad (3.18)$$

This equation now involves quantities which in real space are localized near the surface.

Note that the neglect of ψ^0 and ψ constitutes the semiclassical infinite-barrier model[7, 8] (SCIBM) with $x_0 = 0$. We will show that this approximation is exact in the limit of small $(Q, \vec{k})$ or $(q, \vec{k})$, where Q is an exponential transform variable and q is a cosine transform variable. Formulas relating the cosine transform variable. Formulas relating the cosine transform to the exponential transform in the limit of small Q are given in Appendix A. For the moment we concentrate on the cosine transforms and assume both q and $\vec{k}$ are small in (3.12)–(3.18).

To investigate the long-wavelength behavior of χ, we need the long-wavelength behavior of $\bar{\chi}$ and hence χ^0. We begin with χ^0 and from it derive the properties of $\bar{\chi}$ and hence χ. We assume throughout the discussion that the frequency ω is nonzero; the differences which arise in the zero-frequency case are discussed later.

Consider first the double exponential transform of ψ^0 denoted by $\psi_{QQ'}^0$, which is implicitly a function of $\vec{k}$. At small Q, Q', and k, ψ^0 must vary as

$$\psi_{QQ'}^0 = A k^2 + B Q Q' + \cdots , \qquad (3.19)$$

where A and B are constant numbers which are properties of each material. Since ψ^0 is a piece of the *physical* response function χ^0 which, for example, gives the polarization of the sample as a response to the true electric field, the leading terms must be *analytic*. The terms given above are the leading analytic terms consistent with the assumed symmetry, plus the fact that

$$\lim_{Q \to 0, k \to 0} \psi_{QQ'}^0 = \lim_{Q' \to 0, k \to 0} \psi_{QQ'}^0 = 0 . \qquad (3.20)$$

Equation (3.20) follows from charge conservation—a localized disturbance cannot change the total number of electrons [unless one waits an in-

finite time for more electrons to come from the thermal bath at ∞; we therefore exclude the $\omega = 0$ case where (3.20) does not hold]. Finally we note that the constants A and B are simply proportional to pieces of the polarization induced by a constant (in space) electric field. This polarization is of course a constant finite (when scaled by the sample dimension) number. Any approximation to ψ^0 therefore that produces a nonanalytic term of lower order (i.e., larger) than QQ' or k^2 must be physically incorrect, as it would imply that a finite electric field could produce an infinite polarization in a finite sample.

We note however that the total response function χ does not represent the response to the true electric field, and is not analytic at small $\vec{K}$ in that the leading term is proportional to $k \equiv |\vec{k}| = (k_y^2 + k_z^2)^{1/2}$. This nonanalyticity arises specifically because one piece of the potential $V^{(2)}$ [see (3.11)] has this nonanalyticity at $k \sim 0$, and by parallel momentum conservation $V^{(2)}$ is evaluated at this nonanalytic point in every diagram in Fig. 1(b). It is clear by inspection, however, that the diagrams of Fig. 1(b) are the only ones that have this property.

We eventually want to establish a limiting form for the double exponential transform χ_{QQ} at small K, where $\vec{K} = (Q, \vec{k})$, so that we always consider Q and k to be of the same order of smallness. Although the form (3.19) for ψ^0 was for the exponential transform, all our intermediate equations involve cosine transforms. To make the connection we shall generally use the fact that within a constant factor the two transforms are identical at small Q as discussed in Appendix A, although this must be applied with care because we are not always dealing with localized functions. We note immediately, however, that (3.19) implies that the cosine transform $\psi_{qq'}^0$ goes to zero as k^2 when q or q' is zero, and that it goes to zero *faster* than qq' when k is zero; the latter occurs because the B term in (3.19) obviously cannot appear in the cosine transform. Thus (3.18) implies that the cosine transform $\psi_{qq'}$ has these same limiting properties at small k, q, and q'. Note that ψ^0 goes to zero just fast enough to prevent any trouble from the singular potential factor $V_q \propto (k^2 + q^2)^{-1}$. Thus we have that ψ and ψ^0 have the long-wavelength form

$$\psi_{qq'} \propto k^2 + f(q, q') + \cdots , \qquad (3.21)$$

where

$$\lim_{q \to 0} \frac{f(q, q')}{q} = \lim_{q' \to 0} \frac{f(q, q')}{q'} = 0 , \qquad (3.22)$$

so that specifically f/q^2 is integrable at small q. (Note that our notation is not meant to imply that the function f is the same for ψ as it is for ψ^0.)

To see clearly which terms in χ are important at long wavelengths we substitute (3.17) into (3.12) and (3.13), and rewrite the resulting equation in a way that exhibits all the k and q dependence explicitly:

$$\chi_{qq'} = \chi_q^B \, \underline{1}_{qq'} + \psi_{qq'}/\epsilon_q \epsilon_{q'} - (8\pi e^2/D)k\gamma_q\gamma_{q'} , \quad (3.23)$$

where $\chi_q^B \equiv \chi_q^{0B}/\epsilon_q$ is the susceptibility of a bulk system of the same asymptotic electron density, and where

$$\gamma_q = \frac{\chi_q^B}{k^2+q^2} + \int_0^\infty \frac{d\bar{q}}{2\pi} \frac{\psi_{q\bar{q}}}{(k^2+\bar{q}^2)\epsilon_q\epsilon_{\bar{q}}} \quad (3.24)$$

and

$$D = 1 + 8\pi e^2 \int_0^\infty \frac{d\bar{q}}{2\pi} \frac{k\gamma_q}{k^2+\bar{q}^2} . \quad (3.25)$$

Now the bulk susceptibility χ_q^B goes as k^2+q^2 for small k and q so that the first term in (3.24) goes as a constant. However, it is obvious from the limiting forms (3.21) and (3.22) that the second term in (3.24) goes to zero as k and q go to zero. Similarly, the factor $k/(k^2+\bar{q}^2)$ forces $\bar{q}$ to be small when k is in (3.25) so that the first term in (3.24) can be used for $\gamma_{\bar{q}}$ in (3.25) as well.

We see, therefore, that the final term in (3.23) is of order k at long wavelength and according to (A7) its exponential transform will be of order K. Similarly using (3.21), (3.22), and (A7) on the middle term $\psi_{qq'}/\epsilon_q\epsilon_{q'}$ in (3.23) we find that it is of order K^2 and hence negligible by comparison. We now use (A7) to restore the Fourier exponential transform to the last term in (3.23). The first term in (3.23) is not localized so (A7) cannot be used. However, it is of the form (A8), so that it may be evaluated at long wavelength according to (A13). Putting the pieces together, we have for the diagonal elements of the double exponential transform of χ

$$\chi_{QQ} = \tfrac{1}{2}L\,\chi_Q^B - 2\pi e^2 k(\chi_Q^B/K^2)^2/D \quad (3.26)$$

and

$$D = 1 + 8\pi e^2 \int_0^\infty \frac{d\bar{q}}{2\pi} \frac{k\chi_{\bar{q}}^B}{(k^2+\bar{q}^2)^2} . \quad (3.27)$$

The corrections to (3.26) and (3.27) are of order K^2. Note that the first term of (3.26) is also formally of order K^2 but is also proportional to L which is of order of the sample dimension. We are supposing K to be small with respect to all microscopic inverse lengths, but nevertheless $KL \gg 1$; therefore this first term remains for the time being, but will eventually be subtracted off when we look at the surface term alone. The difference between $\tfrac{1}{2}L$ and the actual length of the sample (equal to $\tfrac{1}{2}L - x_0$) is of course negligible

to the order we are working, and from now we neglect it. [The alert reader may worry about our obtaining a result (3.26) which depends on x_0. One can easily show, however, that to the extent that the point x_0 is outside the charge distribution, the term $x_0 \chi_Q^B$ is exactly cancelled by a contribution from the second term in (3.23).]

As mentioned earlier, the limiting forms given earlier hold only for finite frequency. For example, ψ_{QQ}^0 no longer goes to zero as k, Q, and Q' go to zero, because there is now an infinite time for charge to come in from infinity. Nevertheless, the final conclusion that (3.26) and (3.27) are the limiting forms of χ_{QQ} still holds. This is because the bulk dielectric function no longer goes as a constant but rather $1/\epsilon_q \propto k^2+q^2$. Inspection of Eqs. (3.18), (3.23), (3.24), and (3.25) shows that this factor of $1/\epsilon$ occurs in all the places necessary to make the previous arguments go through at least as strongly as before.

If we now define

$$\chi(\vec{K}, \vec{K}', \omega) = \int d^3x \int d^3x' e^{-i\vec{K}\cdot\vec{x} + i\vec{K}'\cdot\vec{x}'} \chi(\vec{x}, \vec{x}', \omega)$$

$$= A\chi_{QQ'} , \quad (3.28)$$

where A is the area of the surface, we have, after substituting $4\pi e^2\chi^B/K^2 = \epsilon^{-1}(K, \omega) - 1$ and using the fact that $K \to 0$ by assumption, and after performing the integral in (3.27) and substituting in (3.26), that

$$\chi(\vec{K}, \vec{K}, \omega)$$

$$= \frac{K^2}{4\pi e^2} \left[V\left(\frac{1}{\epsilon}-1\right) - A\,\frac{\sin\theta}{K}\left(\frac{1}{\epsilon}-1\right)\frac{1-\epsilon}{1+\epsilon} \right] , \quad (3.29)$$

where $V = A\mathcal{L}$ ($\mathcal{L}$ is the length of the sample) is the volume of the system, and ϵ is the zero wavevector bulk dielectric function

$$\epsilon \equiv \epsilon(0, \omega) = 1 - \omega_p^2/(\omega + i\eta)^2 , \quad (3.30)$$

where η is a positive infinitesimal and ω_p is the bulk plasma frequency of an infinite electron gas of the same asymptotic density ($\omega_p^2 = 4\pi ne^2/m$), and θ is the angle between $\vec{K}$ and the surface normal. We emphasize that (3.29) is exact in the limit of small K, but with $KL \gg 1$. The first term is just the usual bulk term with a pole at the bulk plasma frequency given by $\epsilon = 0$; the second, or surface term has in addition a pole at the surface plasmon frequency given by $\epsilon + 1 = 0$. Thus, Eqs. (3.29) and (3.30) constitute a microscopic proof of the fact, usually and most simply derived from macroscopic considerations, that the surface plasmon frequency is $\omega_p/\sqrt{2}$ at zero wave vector.[20] We leave it as an exercise for the reader to show

that (3.29) can also be derived directly from the semiclassical model Hamiltonians used for example by several authors.[21] Since the derivation of these model Hamiltonians assumes *a priori* that plasmons are the only excitation, (3.29) can be regarded as a proof that $\chi(\vec{K}, \vec{K}, \omega)$ and hence the surface energy is dominated by plasmons in *this* long-wave length limit. Using the same *a priori* assumption, one can also obtain (3.31) and hence (3.30) from sum rules.[22] In Appendix C we show that plasmons are *not* the dominant excitation at large wavelengths in the two-dimensional wave-vector decomposition used by previous authors treating the surface energy problem. Finally we point out that previous work using simple classical image charge arguments would have met with mixed success in obtaining (3.29). Of course the image charge arguments which provide one method of deriving the semiclassical infinite-barrier model (SCIBM) give the correct answer, as (3.26) and (3.27) are the SCIBM results (with the true bulk value of χ^{0B} instead of the RPA value usually used), which we have therefore proved to be exact as $K \to 0$. However, Craig's[4] method seems to give [cf. his Eq. (3.10)] the wrong angular factor in that the $\sin\theta/K$ in (3.29) is replaced by a factor $\delta(K \sin\theta)$.

We now use (3.4) to calculate the dynamic form factor S, and after subtracting off the bulk part [the term $\propto V$ in (3.29)] we find

$$\delta S(\vec{K}, \vec{K}, \omega) = (AK \sin\theta / 4\pi e^2)$$

$$\times [\omega_s \delta(\omega - \omega_s) - \tfrac{1}{2}\omega_p \delta(\omega - \omega_p)],$$

(3.31)

where we have used (3.30) plus the definition $\omega_s = \omega_p / \sqrt{2}$. Therefore

$$N\delta S(\vec{K}) = (AK \sin\theta / 4\pi e^2)(\omega_s - \tfrac{1}{2}\omega_p) .$$

(3.32)

Restoring the coupling-constant dependence explicitly by letting $e^2 \to e^2 \lambda$ in (3.32) (noting that $\omega_s \propto \omega_p \propto e$) and performing the coupling constant integration (2.12) gives

$$\delta E_{xc}(\vec{K}) = (A \sin\theta / K)(\omega_s - \tfrac{1}{2}\omega_p).$$

(3.33)

Finally, on performing the angular average (2.13) we find

$$\delta E_{xc}(K) = (\pi A / 4K)(\omega_s - \tfrac{1}{2}\omega_p).$$

(3.34)

This is the desired exact small-K for which we used in Ref. 13.

To show the relationship between this and the Schmit-Lucas[3] form we substitute (3.33) into (2.15) and perform the Q integration. Remembering that $\vec{K} = (Q, \vec{k})$ we find

$$\delta \bar{E}_{xc}(k) = \tfrac{1}{2}A(\omega_s - \tfrac{1}{2}\omega_p) .$$

(3.35)

This is indeed one contribution to the two-dimensional decomposition $\delta \bar{E}_{xc}$, but it is *not* exact even in the long-wavelength limit $k \to 0$. As we show in Appendix C, *this* latter long-wavelength limit is not dominated by plasmons. Nevertheless, the physics of shifting plasmon zero-point energies is the *sole* contribution to our form (3.34) at small K.

IV. LOCAL-DENSITY APPROXIMATION, THE SHORT-WAVELENGTH LIMIT, AND THE INTERPOLATION SCHEME

In this section we will argue that the local-density approximation (2.16) is correct for $E_{xc}(K)$ at large K, and propose a method of interpolation for the surface contribution $\delta E_{xc}(K)$ between the exact limit (3.34) at small K and the LDA at large K.

Since the LDA is based upon calculations of E_{xc} for a homogeneous electron gas, it will be helpful to review the results of such calculations: the wave-vector decomposition of the exchange energy is

$$E_x^B(K) = N\Theta(2k_F - K)\pi e^2 \left(-\frac{2}{K^2} + \frac{3}{2}\frac{1}{Kk_F} - \frac{1}{8}\frac{K}{k_F^3} \right).$$

(4.1)

The total exchange energy is simply $-N3k_F/4\pi$. In RPA or Hubbard-like approximations, which ignore the frequency and coupling-constant dependence of local-field corrections, the correlation energy has a wave-vector decomposition

$$E_c^B(K) = \frac{1}{2\pi[1 - G(K)]}$$

$$\times \int_0^1 d\Omega \, [\ln a(K, i\Omega) + 1 - a(K, i\Omega)],$$

(4.2)

where

$$a(K, \omega) = 1 - (4\pi e^2 / K^2)[1 - G(K)] \chi_{non}(K, \omega) .$$

(4.3)

$\chi_{non}(K, \omega)$ is the susceptibility of a noninteracting homogeneous electron gas, and $G(K)$ is the local-field correction [$G(K) = 0$ in RPA]. In Appendix E we present a more detailed discussion of bulk correlation-energy calculations and a comparison of numerical results for the total correlation energy in the RPA, Hubbard,[23] Wigner,[24] Noziëres-Pines,[17] and Singwi-Tosi-Land-Sjölander[25] (STLS) approximations.

The $K \to 0$ behavior of $E_{xc}^B(K)$ is determined by the condition[26]

$$\lim_{K \to 0} S_\lambda(K) = \frac{K^2}{2m\omega_p(\lambda n)} ,$$

(4.4)

where $\omega_p(n) = (4\pi n e^2 / m)^{1/2}$. Thus

$$\lim_{K \to 0} E^{B}_{xc}(K) = N \left(-\frac{2\pi e^2}{K^2} + \frac{\omega_p(n)}{2n} \right) . \qquad (4.5)$$

At large K a direct expansion of (4.2) gives the asymptotic behavior

$$\lim_{K \to 0} E^{B}_{xc}(K) = -[1 - G(\infty)] N 8\pi^2 m e^4 \frac{n}{K^6} . \qquad (4.6)$$

A similar result can be obtained directly by second-order perturbation theory, with the quantity in square brackets replaced by $\frac{1}{2}$ (which is also the value it takes in the Hubbard[23] approximation). Since second-order perturbation theory is exact in this limit, we have, at least with respect to (4.6), that $G(\infty) = \frac{1}{2}$ exactly.

The qualitative features of these homogeneous electron gas calculations are revealed in Fig. 2, where we plot the exchange-only form factor

$$S^{B}_{0}(K) - 1 \propto K^2 E^{B}_{x}(K)$$

and compare it with

$$\int_{0}^{1} d\lambda \, S^{B}_{\lambda}(K) - 1 \propto K^2 E^{B}_{xc}(K) .$$

The areas under these curves are, apart from a constant factor, just E^{B}_{x} and E^{B}_{xc}, respectively. It is interesting to note that the inclusion of correlation smooths out the structure factor in K space and increases the relative weight of the large-K fluctuations. This smoothing of the structure factor in K space corresponds to a reduction in the range of the correlation hole (in real space) around each electron.

This reduction in range is of course just the usual screening effect which occurs for the exact correlation function but not the Hartree-Fock approximation to it. It is another reason why we in-
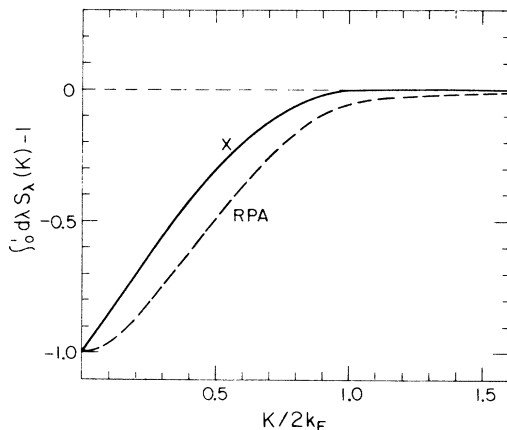
FIG. 2. Structure factor $\int_0^1 d\lambda \, S_\lambda (K) - 1$ for a homogeneous electron gas ($r_s = 4.08$). Solid curve: exchange only. Dashed curve: RPA.

sist on treating E_{xc} as a single entity, particularly with respect to making the local-density approximation, for which we need a short-ranged correlation function for it to make sense. Note also that according to (4.5) and (4.1), it is only $E_{xc}(K)$ for which the leading density-dependent term is the plasmon zero-point energy. The leading term in $E_c(K)$ alone is a plasmon self-energy term whose divergent K^{-1} contribution is exactly cancelled by the K^{-1} term of (4.1). [The $1/K^2$ term in (4.5) is density profile independent, and is therefore irrelevant to the surface problem—it represents the subtraction of the interaction of each electron with itself and is the same for all N-electron systems.] We also know after the fact from our earlier work[13] and from that of Lang and Sham[12] that the LDA is much better for E_{xc} than for E_c alone.

We now consider the LDA (2.16) for inhomogeneous systems. We first show that LDA fails badly for $\delta E_{xc}(K)$, the surface contribution to the exchange-correlation energy, at small K. From (4.5) we find

$$\lim_{K \to 0} \delta E^{LDA}_{xc}(K) = \frac{1}{2} A \int_{-\infty}^{\infty} dx [\omega_p(n(x)) - \omega_p(n_0)\Theta(x - x_0)] .$$

$$(4.7)$$

This is K independent and $n(x)$ dependent, in marked contrast to the exact limit (3.34), which diverges as $K \to 0$. Note that both (4.7) and (3.34) are dominated by shifting plasmon zero point energies.

On the other hand, as we show in Appendix D, the LDA for $\delta E_{xc}(K)$ is exact in the limit of large K, i.e.,

$$\lim_{K \to \infty} \delta E_{xc}(K) = -\frac{1}{2} \frac{8\pi^2 m e^4}{K^6} A$$

$$\times \int_{-\infty}^{\infty} dx [n^2(x) - n_0^2 \Theta(x - x_0)] . \qquad (4.8)$$

From (4.6), we see that (4.8) is just $\lim \delta E^{LDA}_{xc}(K)$ as $K \to \infty$, with $G(\infty) = \frac{1}{2}$. This confirms our intuition that as the wavelength of the fluctuation becomes small, in comparison to other lengths, then the local approximation to its energy must become exact. The actual form (4.8), however, is only numerically valid at very large wave vectors and so it was not used in our calculations except as a check. Instead, in those parts of the calculation relying on the LDA, we use the full expression (2.17).

The interpolation method is now easily described. We define

$$\gamma(K) = 2k_F [4\pi K^2/(2\pi)^3] \delta E_{xc}(K)/A \qquad (4.9)$$

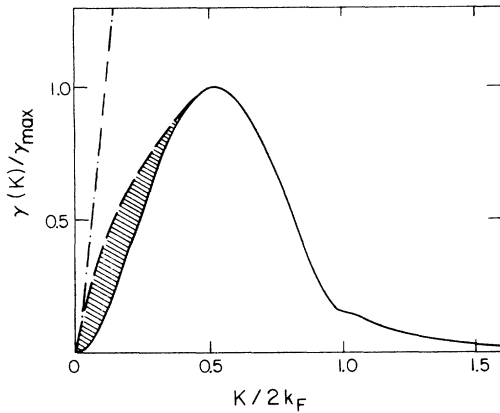so that the exchange-correlation part of the sur-

FIG. 3. Wave-vector analysis of the surface energy $\delta E_{xc} = A \int d(K/2k_F) \gamma(K)$ in the RPA using density profiles for the infinite-barrier model. Solid curve: LDA; dash-dotted line: exact asymptote (4.11); dashed arc: interpolation. $(r_s = 4.$ For $r_s = 2.07$ and 6, see Ref. 13.) Here $\gamma_{max} = 291$ erg/cm^2.

face energy is just

$$A \int_0^\infty d\left(\frac{K}{2k_F}\right) \gamma(K) . \tag{4.10}$$

[Note that $\gamma(K)$ is, apart from a K-independent factor, just the spherical average of $\int_0^1 d\lambda \, \delta S_\lambda(\vec{K})$.] From the exact limit (3.34) we find

$$\lim_{K \to 0} \gamma(K) = \frac{k_F K}{4\pi} (\omega_s - \tfrac{1}{2}\omega_p) . \tag{4.11}$$

We compute $\gamma^{LDA}(K)$ by (2.16), and then interpolate.

The interpolation scheme we have used is an arbitrary but well-defined procedure which reproduces more or less the results of "interpolation by eye": we define γ_{max} to be the maximum value of $\gamma^{LDA}(K)$, and plot $\gamma^{LDA}(K)$ vs $K/2k_F$ on a "normalized" scale such that the points $(K/2k_F = 1$, $\gamma^{LDA} = 0)$ and $(K/2k_F = 0, \gamma^{LDA} = \gamma_{max})$ are equidistant from the origin. We also plot the straight line corresponding to the initial slope of $\gamma(K)$ from (4.11), and interpolate between the two curves via the arc of that circle which is tangent to the straight line at $K = 0$ and to $\gamma^{LDA}(K)$ at some larger value of K. The construction is shown in Figs. 3 and 4.

(In Ref. 13 we used the same interpolation scheme, except that we did not worry about the precise "normalization" of the vertical axis, which has been introduced here only to make the scheme mathematically well defined. The small differences between the numbers here and in Ref. 13 are due mainly to numerical refinements and not to the change in "normalization." Doubling the "normalization" changes the interpolation cor-

rection by 7% or less.)

The result of the interpolation is to pick up a small positive contribution (beyond the LDA) to the surface exchange-correlation energy (namely the hatched areas in Figs. 3 and 4) from the region of small K.

V. RESULTS AND DISCUSSION

As a proving ground for the interpolation scheme proposed in Sec. IV, we consider the infinite-barrier model (IBM) of a metal surface, in which the single-particle wave functions [associated with the noninteracting Hamiltonian

$$T + \int d^3x \, v_0(\vec{x}) n(\vec{x})$$

of Sec. II] take a particularly simple form. Harris and Jones[8] have evaluated the surface exchange energy for this (non-self-consistent) model, and Wikborg and Inglesfield[9] have calculated the surface correlation energy within RPA.

Numerical results for the IBM are presented in Table I and Fig. 3. Note that the LDA gives a surface exchange energy about 50% larger than the exact value, and a surface exchange-correlation energy about 10% smaller than the exact value. (A similar comparison between LDA and exact results for the IBM has been performed by Lang and Sham,[12] who however compared the Wigner approximation for the LDA calculation with the RPA for the exact solution.) Thus the LDA is better for exchange and correlation than for exchange alone, as anticipated by the argument of Sec. IV. Moreover the results of the interpolation scheme are
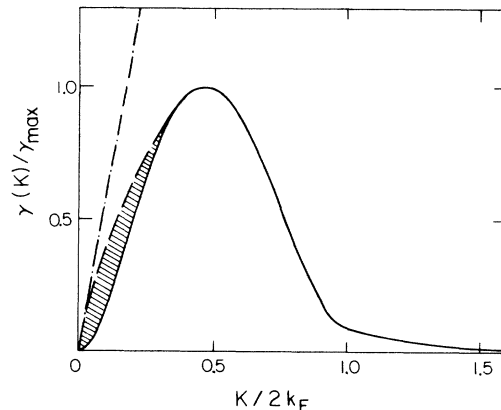

FIG. 4. Wave-vector analysis of the surface energy in the Hubbard approximation using Lang-Kohn density profiles. Solid curve: LDA; dash-dotted line: exact asymptote (4.11); dashed arc: interpolation. $(r_s = 4.$ For $r_s = 2$ and 6, see Ref. 13.) Here $\gamma_{max} = 450$ erg/cm^2.

TABLE I. Exchange-correlation contribution to the surface energy (erg/cm^2) in the infinite-barrier model. x, exchange; xc, exchange + correlation.

	x	xc
$r_S = 2.07$		
RPA LDA	1107	1241
RPA interpolation	$\cdots$	1365
RPA exact	700	1388
$r_S = 4$		
RPA LDA	153	184
RPA interpolation	$\cdots$	204
RPA exact	100	203
$r_S = 6$		
RPA LDA	45	58
RPA interpolation	$\cdots$	64
RPA exact	30	63

within 2% of the exact values, and so can be regarded as essentially exact. {The figures quoted as "RPA exact" are based on a private communication from J. E. Inglesfield of a refined calculation of the integrations from $k = 0$ to $2k_F$, to which we have added the "tail area" above $2k_F$ as given by the LDA [see Eq. (2.15)].}

A possible objection to our IBM test of the interpolation method is that the IBM density profile varies more rapidly in space than do the more physical profiles obtained from self-consistent calculations. In order to meet this objection we have made a numerical comparison of the interpolation correction with the first gradient correction[16] to the exchange-correlation energy for a class of density profiles which vary so slowly that the accuracy of the gradient expansion cannot be

doubted. We have found good agreement between the two methods in this limit; details will be published elsewhere.[27]

Now, armed with some confidence in the correctness of the interpolation scheme, we proceed to the more realistic surface-density profiles calculated by Lang and Kohn[1] for the self-consistent jellium model. Numerical results are presented in Tables II and III and Fig. 4. For the interpolation scheme we have used the Hubbard[23] approximation, the most realistic approximation for which we have a simple wave-vector decomposition $E_c^B(K)$. Note that at $r_s = 6$ the LDA is again 10% too small, while at $r_s = 2$, where the density profile varies more slowly on the scale of r_s, the LDA is, as expected, much closer to the "exact" value found by interpolation. Table II also shows a comparison of δE_{xc} as calculated in the LDA using the RPA, Hubbard,[23] Wigner,[24] and STLS[25] approximations.

We note that our results for δE_{xc} are not quite self-consistent, in that the Lang-Kohn density profiles are calculated with an effective exchange-correlation potential

$$v_{xc}(\bar{x}) = [\delta/\delta n(\bar{x})]E_{xc} , \qquad (5.1)$$

which assumes the validity of the LDA (and the Wigner approximation). While our interpolation scheme does define a nonlocal density functional for E_{xc}, the evaluation of its functional derivative (5.1) is impossible. It is, of course, possible to adopt a variational form for the density $n(x)$ or equivalently for the effective one-electron potential $v_0(x)$, and so minimize the total energy, including nonlocal exchange and correlation. We have done this[27] and found that corrections to the LDA density profile are negligible, as we anticipated in Ref. 13, because the "extra area" introduced by interpolation is small and the exact $K \to 0$

TABLE II. Exchange-correlation energy of the jellium surface (erg/cm^2). The column marked xc shows the value of the indicated density functional for $E_{xc}[n(x)]$ with the density profiles $n(x)$ equal to those given by Lang and Kohn (Ref. 1). The column marked xc-sc shows the fully self-consistent value of $E_{xc}[n(x)]$, with the density profile $n(x)$ calculated by minimization of the functional being evaluated, except that, as discussed in the text, the interpolation correction is calculated using the Hubbard-LDA profile. (The RPA and Hubbard approximations have been parametrized in the xc-sc calculations.)

Functional	$r_s = 2$		$r_s = 4$		$r_s = 6$	
	xc	xc-sc	xc	xc-sc	xc	xc-sc
Exchange only LDA	3070	$\cdots$	225	$\cdots$	44	$\cdots$
Wigner LDA	3250	3250	260	260	55	55
RPA LDA	3435	3390	272	266	57	54
STLS LDA	3400	$\cdots$	268	$\cdots$	54	$\cdots$
Hubbard LDA	3380	3345	264	262	54	54
Hubbard interpolation	3555	3520	284	282	59	59

TABLE III. LDA and interpolation correction to the exchange-correlation energy of the jellium surface (erg/cm^2) as a function of r_s. (Parametrized Hubbard approximation.)

r_s	LDA	Correction
2	3345	173
2.5	1490	87
3	762	49
4	262	20
5	111	10
6	54	5

limit of $\delta E_{xc}(K)$ depends only on the bulk density and not on the density profile.

When the wave-vector interpolation method for the exchange-correlation part of the surface energy is combined with a nonperturbative treatment of the short-range part of the ionic potential,[28] the resulting calculated surface energies for simple metals are in good agreement with experiment. (Details will be published later.)

In conclusion, the local-density approximation for E_{xc} (but not for E_x alone) is surprisingly good even for the strong inhomogeneity associated with a metal surface. Under a decomposition of E_{xc} into contributions $E_{xc}(K)$ from fluctuations of different wave vector K, we find that LDA is correct at large K and fails badly at small K, but this failure is rather unimportant because of the phase-space factor $4\pi K^2$. Moreover, for the surface problem we have derived the exact behavior (including all many-body effects) of $\delta E_{xc}(K)$ [and also $\chi(\vec{K}, \omega), S(\vec{K}, \omega)$] at small K, and have proposed an interpolation scheme for $\delta E_{xc}(K)$ which, when tested against RPA calculations for the infinite-barrier model, proves to be essentially exact.

ACKNOWLEDGMENT

APPENDIX A: DEFINITIONS OF TRANSFORMS AND SOME LIMITING CASES

In general we adopt as our complete set of functions (for expanding wave functions, potentials, etc.) the usual imaginary exponentials $e^{i\vec{K}\cdot\vec{x}}$, where $\vec{K}$ is quantized with periodic boundary conditions on an almost infinite cube of side L, centered about the origin. For the variations perpendicular to the physical surface [which we take to be in the vicinity of $x = x_0$, where $\vec{x} = (x, y, z)$] it will be more convenient to work with the linear combinations

$$C_q(x) = (e^{iqx} + e^{-iqx})\Theta(x) = (2\cos qx)\Theta(x), \quad (A1)$$

where as usual $\vec{K} = (q, \vec{k})$, and where in particular $q = (2\pi/L)n$; $n = 0, \pm1, \pm2, \ldots$. We define the cosine transform therefore of the function $F(x)$ as

$$F_q^c = \int_0^{L/2} dx\, C_q(x)F(x), \quad (A2a)$$

with the inverse transformation given (for $x > 0$) by

$$F(x) = \sum_q C_q(x)F_q^c, \quad (A2b)$$

where the sum over q is *defined* to mean

$$\sum_q f_q \equiv \frac{1}{L}\left(\tfrac{1}{2}f_0 + \sum_{n=1}^{\infty} f_{2\pi n/L}\right). \quad (A3a)$$

We will almost never make use of the discrete nature of the sum, which in the limit of large L may be replaced by an integral in the usual way

$$\sum_q f_q = \int_0^{\infty} \frac{dq}{2\pi} f_q + O(L^{-2}). \quad (A3b)$$

We note that

$$\sum_q C_q(x)C_q(x') = \delta(x - x')\Theta(x)\Theta(x'), \quad (A4a)$$

$$\int_0^{L/2} dx\, C_q(x)C_{q'}(x) = L(\delta_{q,q'} + \delta_{q,-q'}) \equiv 1_{qq'}, \quad (A4b)$$

where $\delta_{q,q'} = 1$ for $q = q'$ and zero otherwise. The combination $1_{qq'} \equiv L(\delta_{q,q'} + \delta_{q,-q'})$ acts as the unit matrix in this space as it has the property that

$$\sum_{\bar{q}} 1_{q\bar{q}} G_{\bar{q}q'} = \sum_{\bar{q}} G_{q\bar{q}} 1_{\bar{q}q'} = G_{qq'} \quad (A5)$$

for an arbitrary double cosine transform $G_{qq'}$.

We now go on to derive a few properties. First we need the relationship between the cosine transform and the ordinary exponential transform

$$F_q \equiv \int_{-L/2}^{L/2} dx\, e^{-iqx}F(x) \quad (A6)$$

at small q (but still $q \gg L^{-1}$). This is trivially given by

$$F_q = \tfrac{1}{2}F_q^c - i\int_{-\infty}^{\infty} dx\, \sin qx F(x) = \tfrac{1}{2}F_q^c + O(q), \quad (A7)$$

where we have assumed that F is localized near the surface, so that one can extend the integral limits to ∞ and then expand for small q, and we have further assumed that $F = 0$ for $x < 0$.

We will also need the expression for the small-Q form of the double exponential transform G_{QQ} of a function $G(x, x')$ whose double cosine transform is

$$G_{qq'} = L\mathcal{F}_q(\delta_{qq'} + \delta_{q,-q'}) \equiv \mathcal{F}_q 1_{qq'}, \quad (A8)$$

where $\mathcal{F}_q$ is the exponential transform of an even

function $\mathfrak{F}(x)$. Equation (A8) illustrates a feature of our notation in that the superscript "c" will generally be omitted for a *double* cosine transform; it is distinguished from the exponential transform by the use of lower case indices, i.e.,

$$G_{qq'} \equiv \int_0^{L/2} dx \int_0^{L/2} dx' C_q(x) C_{q'}(x') G(x, x') \quad \text{(A9)}$$

and

$$G_{QQ'} \equiv \int_{-L/2}^{L/2} dx \int_{-L/2}^{L/2} dx' e^{-iQx+iQ'x'} G(x, x'). \quad \text{(A10)}$$

However, the notation of (A2) and (A6) will still be used for single transforms: $\mathfrak{F}_q$ and $\mathfrak{F}_Q$ are both exponential transforms while $\mathfrak{F}_q^c$ and $\mathfrak{F}_Q^c$ are both cosine transforms.

Since the function $G(x, x')$ corresponding to (A8) is not localized in both x and x' together, we cannot use (A7) to find the desired limiting form. Inserting (A8) in the inverse transform of (A9) we easily find, however,

$$G(x, x') = [\mathfrak{F}(x - x') + \mathfrak{F}(x + x')]\Theta(x)\Theta(x'), \quad \text{(A11)}$$

where $\Theta(x) = 1$ for $x > 0$ and zero otherwise. Now we insert (A11) in (A10) with $Q = Q'$, and after straightforward algebraic manipulation which makes use of the fact that $\mathfrak{F}(x) = \mathfrak{F}(-x)$, we find

$$G_{QQ} = \frac{1}{2} \int_{-L/2}^{L/2} dx \int_{-L/2}^{L/2} dx' e^{-iQ(x-x')} \mathfrak{F}(x - x')$$

$$+ 2 \int_0^{L/2} dx \int_0^{L/2} dx' \sin Qx \sin Qx' \, \mathfrak{F}(x + x').$$

$$\text{(A12)}$$

Since $\mathfrak{F}$ is taken to be a localized function of its argument, we now have G_{QQ} in a form where the large L limit can easily be performed: The first term becomes $\frac{1}{2}L\mathfrak{F}_Q$; while the second term remains unchanged except that the upper limits of both integrals now go to ∞. Therefore, at small Q we have

$$G_{QQ} \to \frac{1}{2}L\mathfrak{F}_Q + O(Q^2) \quad \text{(A13)}$$

which is the desired limiting form.

APPENDIX B: REDUCTION OF INTEGRAL EQUATION FOR χ

Here we use (3.7) along with the definition (3.8)–(3.11) to derive Eqs. (3.12)–(3.14). We write (3.7) as

$$\chi = \chi^0(1 + V^{(2)}\chi) + \chi^0 V^{(1)}\chi, \quad \text{(B1)}$$

where $V^{(1)}$ and $V^{(2)}$ are given by (3.11). Equation (B1) can be written symbolically as

$$\chi = [(1 - \chi^0 V^{(1)})^{-1}\chi^0](1 + V^{(2)}\chi). \quad \text{(B2)}$$

Defining $\tilde{\chi}$ to be the quantity in square brackets in (B2) leads to

$$\tilde{\chi} = \chi^0 + \chi^0 V^{(1)}\tilde{\chi}, \quad \text{(B3)}$$

which is the same as Eq. (3.14) in matrix notation. Writing (B2) in terms of $\tilde{\chi}$ gives

$$\chi = \tilde{\chi} + \tilde{\chi} V^{(2)}\chi. \quad \text{(B4)}$$

Because $V^{(2)}$ is a factorizable interaction (B4) may be solved exactly if $\tilde{\chi}$ is given. In Dirac notation we write $V^{(2)}$ as $-|v\rangle \alpha \langle v|$ where $|v\rangle$ and $\langle v|$ are the respective column and row vectors that have the elements v_q. Then (B4) becomes

$$\chi = \tilde{\chi} - \tilde{\chi}|v\rangle \alpha \langle v|\chi. \quad \text{(B5)}$$

This is solved in the usual way by multiplying by $|v\rangle$, yielding

$$\chi|v\rangle = \tilde{\chi}|v\rangle - \tilde{\chi}|v\rangle \alpha \langle v|\chi|v\rangle, \quad \text{(B6)}$$

which is now a set of uncoupled algebraic equations for each element of $\chi|v\rangle$. We have trivially

$$\chi|v\rangle = \tilde{\chi}|v\rangle/D, \quad \text{(B7)}$$

where

$$D = 1 + \alpha \langle v|\tilde{\chi}|v\rangle. \quad \text{(B8)}$$

Upon substitution of (B7) back in (B5) we find

$$\chi = \tilde{\chi} - \tilde{\chi}|v\rangle(\alpha/D)\langle v|\tilde{\chi}. \quad \text{(B9)}$$

Equations (B8) and (B9) are the respective matrix versions of Eqs. (3.13) and (3.12).

APPENDIX C: TWO-DIMENSIONAL WAVE-VECTOR DECOMPOSITION

Here we consider the exchange-correlation energy as a function of the *two-dimensional* wave vector. From (2.15), (2.12), and (3.4) we have that this quantity is given by

$$\bar{E}_{xc}(k) = \left(\int_0^\infty \frac{d\omega}{2\pi}(-2)\,\mathrm{Im} \int_0^1 \frac{d\lambda}{\lambda} \sum_{qq'} \frac{1}{2} V_{qq'}\chi_{q'q} \right) - \frac{N\alpha}{2}, \quad \text{(C1)}$$

where $V_{qq'}$ is given by (3.9), $\chi_{qq'}$ by (3.12), and α by (3.10a). Making these latter substitutions and using (3.13) gives

$$\bar{E}_{xc}(k) = \left\{ \int_0^\infty \frac{d\omega}{2\pi}(-2)\,\mathrm{Im} \int_0^1 \frac{d\lambda}{\lambda} \frac{1}{2}\left[\sum_q \alpha v_q \tilde{\chi}_{qq} - \sum_{q\tilde{q}q'} \frac{\alpha^2}{D} v_{\tilde{q}} \tilde{\chi}_{\tilde{q}q} v_q \tilde{\chi}_{q\tilde{q}'} v_{\tilde{q}'} + \left(\frac{1}{D} - 1\right) \right] \right\} - \frac{N\alpha}{2}, \quad \text{(C2)}$$

where D is given by (3.13).

Now consider the small-k limit. First, we can use the same arguments as in Sec. III to show that D, and hence $(1/D - 1)$, can be evaluated using just the first term of (3.16), so that D is given by (3.27) which becomes independent of the surface profile as $k \to 0$. Similarly, the second term in (C2) can be shown to be independent of the density profile as $k \to 0$. To show this we begin by writing (3.17) as

$$\bar{\chi}_{qq'} = \chi_q^B \underline{1}_{qq'} + \phi_{qq'}, \tag{C3}$$

where χ_q^B is the bulk susceptibility χ_q^{0B}/ϵ_q and

$\phi_{qq'} = \psi_{qq'}/\epsilon_q \epsilon_{q'}$. We now count powers of k, noting that $\alpha \propto k^{-1}$ and $v_q \propto k$. We see that this expression is formally of order k and hence is nonvanishing at $k \to 0$ only if the integrals are sufficiently singular at $q = 0$. By referring to the forms of χ_q^{0B} and $\psi_{qq'}$ (and hence χ_q^B and $\phi_{qq'}$) we see that this happens only when both factors of $\bar{\chi}$ are proportional to $\underline{1}_{qq'}$; thus only the profile-independent first term of (C3) comes into play in the limit. Finally, the first term in (C2) is of order k^0. Thus even in the $k = 0$ limit the profile dependent $\phi_{qq'}$ term survives. In particular the first term of (C2) becomes in the large-L limit

$$\int_0^\infty \frac{d\omega}{2\pi}(-2)\,\mathrm{Im}\int_0^1 \frac{d\lambda}{\lambda}\,\frac{1}{2}\left(L\int_0^\infty \frac{dq}{2\pi}\alpha v_q \chi_q^B + \tfrac{1}{2}\alpha v_0 \chi_0^B + \sum_q \alpha v_q \phi_{qq}\right). \tag{C4}$$

Using the identity $L = 2(\mathcal{L} + x_0)$, where $\mathcal{L}$ is the length of the sample, and subtracting the "volume" contribution to the large parentheses in (C4),

$$\mathcal{L}\int_{-\infty}^\infty \frac{dq}{2\pi}\alpha v_q \chi_q^B, \tag{C5}$$

gives (since χ_q^B and v_q are even functions of q)

$$\int_0^\infty \frac{d\omega}{2\pi}(-2)\,\mathrm{Im}\int_0^1 \frac{d\lambda}{\lambda}\,\frac{1}{2}\left(x_0\int_{-\infty}^\infty \frac{dq}{2\pi}\alpha v_q \chi_q^B + \tfrac{1}{2}\alpha v_0 \chi_0^B + \sum_q \alpha v_q \phi_{qq}\right). \tag{C6}$$

Therefore the total contribution to $\delta\bar{E}_{xc}(k)$ is

$$\delta\bar{E}_{xc}(k) = \int_0^\infty \frac{d\omega}{2\pi}(-2)\,\mathrm{Im}\int_0^1 \frac{d\lambda}{\lambda}\,\frac{1}{2}\left(x_0\int_{-\infty}^\infty \frac{dq}{2\pi}\alpha v_q \chi_q^B + \sum_q \alpha v_q \phi_{qq}\right) + \delta\bar{E}_{xc}^{\mathrm{SCIBM}}(k), \tag{C7}$$

where

$$\delta\bar{E}_{xc}^{\mathrm{SCIBM}}(k) = \int_0^\infty \frac{d\omega}{2\pi}(-2)\,\mathrm{Im}\int_0^1 \frac{d\lambda}{\lambda}\,\frac{1}{2}\left[\frac{1}{2}\alpha v_0 \chi_0^B - \int_0^\infty \frac{dq}{2\pi}\alpha^2 v_q^3 \frac{(\chi_q^B)^2}{D} + \left(\frac{1}{D}-1\right)\right] \tag{C8}$$

is the value obtained in the semiclassical infinite-barrier model, and which is independent of the surface-density profile. Note the presence of the manifestly profile dependent term in the large parentheses of (C7) which survives the $k \to 0$ limit. We thus see quite clearly that semiclassical model is not exact in *this* $k \to 0$ limit, even though it gives D and hence the plasmon frequencies exactly.

APPENDIX D: LARGE-K LIMIT FOR THE SURFACE PROBLEM

In this section we evaluate $\delta E_{xc}(K)$ [see Eq. (2.13)] for the surface problem, in the limit of large K, and show that in this limit the local-density approximation is correct.

We begin by considering the susceptibility χ, since through Eqs. (3.4) and (2.12) we can express $E_{xc}(K)$ in terms of this. It is given in matrix notation by Eq. (3.7). We note that except for a negligible region of K space, large $\bar{K}$ implies large

$\bar{k}$ [$\bar{K} = (Q, \bar{k})$] so that there is necessarily a large momentum transfer through the Coulomb interaction in the iterative expansion, which means that V is small, and so it suffices to take the leading term:

$$\chi \simeq \chi^0 + \chi^0 V \chi^0. \tag{D1}$$

Similarly, the average momentum transfer through V in the internal structure of χ^0 [see Fig. 1(b)] is also small. Therefore to first order in V we may take $\chi^0 = \chi^{\mathrm{non}}$ in the second term of (D1), where χ^{non} is the susceptibility of a noninteracting system with the same density profile as the true one, and is given by the first diagram on the right-hand side of Fig. 1(a). In the first term in (D1) we must expand χ^0 and hence keep the first two terms of Fig. 1(a), where now the wiggly line can be replaced by a bare Coulomb interaction. Thus we write[29]

$$\chi \simeq \chi^{\mathrm{non}} + \chi^{\mathrm{non}} V \chi^{\mathrm{non}} + \delta\chi, \tag{D2}$$

where $\delta\chi$ is this second term of Fig. 1(a), and whose contribution to the energy is known as the second-order exchange term. The second term in (D2) makes a contribution to the energy known as the second-order direct term, while the first term gives the Hartree-Fock term or exchange energy.

It is most convenient to work in a representation in which functions are Fourier transformed parall-

el to the surface, i.e.,

$$F_{\mathfrak{k}}(x, x') = \int d^2 x_{\shortparallel} e^{-i\vec{\mathfrak{k}}\cdot(\vec{x}-\vec{x}')} F(\vec{x}, \vec{x}') \tag{D3}$$

for an arbitrary function F. We have therefore for the Coulomb potential

$$V_{k}(x, x') = (2\pi e^2/k)e^{-k(x-x')} \tag{D4}$$

and

$$\chi_k^{\text{non}}(x, x') = \frac{1}{A} \sum_{q_1 q_2 \vec{k}_1, \sigma} f_{q_1, \vec{k}_1}(1 - f_{q_2, \vec{k}_1 + \vec{k}}) \phi_{q_1}^*(x) \phi_{q_2}(x) \phi_{q_2}^*(x') \phi_{q_1}(x')$$

$$\times \left(\frac{1}{\omega + i\eta - \epsilon_{q_2, \vec{k}_1 + \vec{k}} + \epsilon_{q_1, \vec{k}_1}} - \frac{1}{\omega + i\eta + \epsilon_{q_2, \vec{k}_1 + \vec{k}} - \epsilon_{q_1, \vec{k}_1}} \right), \tag{D5}$$

where $\phi_q(x)$ is the "perpendicular part" of the single-particle wave functions ψ, that is,

$$\psi_{q\vec{k}}(\vec{x}) = \phi_q(x)e^{i\vec{k}\cdot\vec{x}}/A^{1/2} \tag{D6}$$

and $\epsilon_{q\vec{k}}$ is the single-particle energy which to zeroth order[29] in V is given by

$$\epsilon_{q\vec{k}} = (k^2 + q^2)/2m . \tag{D7}$$

Note that $\vec{k}$ is always parallel to the surface and A is the surface area.

Consider now the contribution to the exchange energy, which is

$$E_x(\vec{K}) = A \int dx \int dx' e^{-iQ(x-x')} \tfrac{1}{2} V_k(x, x') \left(\int_0^\infty \frac{d\omega}{2\pi} [-2\,\text{Im}\chi_k^{\text{non}}(x, x', \omega)] - \langle n(\vec{x})\rangle \delta(\vec{x} - \vec{x}') \right) \tag{D8}$$

We note that for $k > 2k_f$ the factor $1 - f_{q_2, \vec{k}_1 + \vec{k}}$ in (D5) may be replaced by unity. After doing the integral indicated in (D8) one sees that the only dependence on the dummy variable q_2 left in (D5) is in $\phi_{q_2}(x)$ and $\phi_{q_2}^*(x')$, so that the completeness relation

$$\sum_{q_2} \phi_{q_2}^*(x') \phi_{q_2}(x) = \delta(x - x') \tag{D9}$$

may be used to perform the q_2 sum, and we are left with

$$E_x(\vec{K}) = \int dx\, \tfrac{1}{2} V_k(x, x) \left(\sum_{q_1 k_1 \sigma} f_{q_1, \vec{k}_1} |\phi_{q_1}(x)|^2 - n(\vec{x}) \right)$$

$$= 0 . \tag{D10}$$

Thus there is no exchange contribution at large K, and we turn next to the second-order contributions.

To do this we again replace the factor $(1 - f_{q_2, \vec{k}_1 + \vec{k}})$ in the parentheses of (D5) by unity, and also neglect $q_1^2/2m$ in the energy denominators because it gets compared to k^2 which is large. Note however that $q_2^2/2m$ cannot be neglected, because its range is unrestricted by the Fermi factors and is likely to be just as large as $k^2/2m$. Equation (D5) for χ^{non} can thus be written

$$\chi_k^{\text{non}}(x, x') = \frac{1}{A} \sum_{q_1 \vec{k}_1 \sigma} f_{q_1, \vec{k}_1} \phi_{q_1}^*(x) \phi_{q_1}(x')$$

$$\times [G_{x, x'}(\Omega_k^+) + G_{x, x'}(\Omega_k^-)], \tag{D11}$$

where

$$G_{x, x'}(\Omega) = \sum_{q_2} \frac{\phi_{q_2}(x) \phi_{q_2}^*(x')}{\Omega - q_2^2/2m} \tag{D12}$$

is just the Green's function for the reduced one-dimensional single-particle eigenvalue problem perpendicular to the surface and where

$$\Omega_k^\pm = \pm(\omega + i\eta) - k^2/2m . \tag{D13}$$

Note that $q_1^2/2m$, and $\vec{k}_1 \cdot \vec{k}/m$ have been dropped, because they are much smaller by assumption than $k^2/2m$. We now note that large k means large Ω on the average. Finally in large-Ω limit the Green's function (D12) becomes simply the free-particle Green's function, which is

$$\propto (1/\Omega^{1/2})e^{-\Omega^{1/2}|x-x'|} . \tag{D14}$$

We cannot simply replace (D14) by a sort of δ function, even though it is high peaked at $x \sim x'$ for large Ω, because in the evaluation of the second-order exchange energy it gets multiplied by other similarly singular factors. We can, however, set $x = x'$ in other slowly varying terms that

multiply it, such as $\phi_{q_1}^*(x)\phi_{q_1}(x')$ in (D11); this is necessarily slowly varying because of the Fermi factor $f_{q_1,\vec{k}_1}$. Making this replacement, and noting that the particle density $n(x)$ is given by

$$n(x) = \frac{1}{A} \sum_{q_1 k_1 \sigma} |\phi_{q_1}(x)|^2 f_{q_1,\vec{k}_1},$$

we have

$$\chi_k^{non}(x, x') \to n[\tfrac{1}{2}(x+x')][G_{xx'}(\Omega_k^+) + G_{xx'}(\Omega_k^-)], \quad (D15)$$

with $\phi_{q_2}(x)$ in $G_{xx'}$ replaced by free-particle functions $\propto e^{iq_2 x}$.

We now evaluate the second-order direct term which arises from the second term in (D2). This is

$$E_{2,direct}(\vec{K}) = \tfrac{1}{2}A \int dx \int dx' \, e^{-iQ(x-x')} \tfrac{1}{2} V_k(x, x')(-2) \text{Im} \int_0^\infty \frac{d\omega}{2\pi} \int d\bar{x} \int d\bar{x}' \, \chi_k^{non}(x, \bar{x}) V_k(\bar{x}, \bar{x}') \chi_k^{non}(\bar{x}', x'), \quad (D16)$$

where we have used (D2), (2.12), and (3.4). The over-all factor of $\tfrac{1}{2}$ comes from the coupling-constant integration, which as usual is carried out in the presence of an external potential so that the wave functions ϕ remain independent of coupling constant. We now substitute (D15) into (D16) and evaluate. In doing so, we note that according to (D4) the potential V_k is sharply peaked around $x \sim x'$, just as $G_{xx'}$ is. Thus in evaluating (D16) it becomes irrelevant at sufficiently large k whether we evaluate the prefactor n in (D15) at $x, x', \bar{x}$, or $\bar{x}'$, and we use this flexibility and find after some algebra that

$$E_{2,direct}(K) = -\frac{8\pi^2 me^4}{K^6} A \int_{-\infty}^\infty dx \, n^2(x) \quad (D17)$$

and

$$\delta E_{2,direct}(K) = -\frac{8\pi^2 me^4}{K^6} A \int_{-\infty}^\infty dx \, [n^2(x) - n_0^2(x)], \quad (D18)$$

where as before $|e|n_0(x)$ is the charge distribution of the uniform jellium background. Note that no spherical averaging [Eq. (2.13)] was necessary, since (D17) is spherically symmetric already.

We are now left with the evaluation of the second-order exchange term which comes from the last term in (D2). This is done with exactly the same arguments which we just used to produce (D18). Thus we give only the final result

$$\delta E_{2,exch}(K) = -\tfrac{1}{2}\delta E_{2,direct}(k). \quad (D19)$$

Thus we have that δE_{xc} is given by

$$\delta E_{xc}(K) = -\frac{4\pi^2 me^4}{K^6} A \int_{-\infty}^\infty dx \, [n^2(x) - n_0^2(x)]. \quad (D20)$$

This is manifestly a local function of the density. According to Eq. (4.6) it is also precisely what is predicted by the LDA [noting that $G(\infty) = \tfrac{1}{2}$].

APPENDIX E: CORRELATION ENERGY OF A HOMOGENEOUS ELECTRON GAS

From (2.6), (3.3), and (3.4) we have

$$E_c = \int \frac{d^3K}{(2\pi)^3} \frac{1}{2} \int_0^1 d\lambda \frac{4\pi e^2}{K^2}$$

$$\times \int_0^\infty d\omega \left(-\frac{1}{\pi} \text{Im}\chi_\lambda(K, \omega) + \frac{1}{\pi}\chi_{non}(K, \omega) \right), \quad (E1)$$

TABLE IV. Correlation energy (Ry/electron) of the homogeneous electron gas in various approximations.

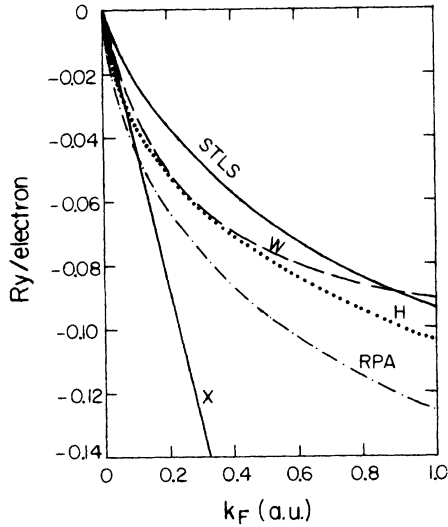| r_s	RPA	Hubbard	Nozières-Pines (Ref. 17)	Wigner	STLS
0.001	−0.57	···	−0.33	−0.11	···
0.01	−0.43	···	−0.26	−0.11	···
0.1	−0.29	···	−0.19	−0.11	···
1	−0.158	−0.131	−0.115	−0.100	−0.124
2	−0.124	−0.102	−0.094	−0.090	−0.092
3	−0.106	−0.087	−0.081	−0.081	−0.075
4	−0.094	−0.077	−0.072	−0.075	−0.064
5	−0.085	−0.069	−0.065	−0.069	−0.056
6	−0.078	−0.064	−0.059	−0.064	−0.050
10	−0.061	−0.051	−0.044	−0.049	−0.036
20	−0.043	−0.035	−0.022	−0.032	−0.022

FIG. 5. Correlation energy per electron of a homogeneous electron gas. RPA, Wigner (W), Hubbard (H), and STLS approximations. X is the exchange energy per electron, for comparison.

where χ_{non} is the noninteracting susceptibility. In RPA or Hubbard-like[23] theories

$$\chi_\lambda(K, \omega) = \frac{\chi_{non}(K, \omega)}{1 - \lambda(4\pi e^2/K^2)[1 - G(K)]\chi_{non}(K, \omega)} , \quad \text{(E2)}$$

with the λ and ω dependence of the local-field correction $G(K)$ igonored [RPA $G(K) = 0$, Hubbard $G(K) = \frac{1}{2}K^2/(K^2 + k_F^2)$]. The coupling-constant integration is trivially performed, with the result

$$E_c = \int \frac{d^3K}{(2\pi)^3} \frac{1}{2\pi[1 - G(K)]}$$

$$\times \int_0^\infty d\omega \, \text{Im}[\ln a(K, \omega) + 1 - a(K, \omega)] , \quad \text{(E3)}$$

with $a(K, \omega)$ given by (4.3). The direct integration

of (E3) along the real ω axis permits one to separate out plasmon and particle-hole contributions. However, the numerical integration is more easily performed along the imaginary ω axis as discussed by Pines,[30] with the result (4.2). Note that

$$a(K, i\Omega) = 1 + \{4[1 - G(K)]/\pi k_F x^2\}[\tfrac{1}{2} + w(x, y)] , \quad \text{(E4)}$$

$$w(x, y) = \frac{1}{16x^3}(y^2 + 4x^2 - x^4)\ln\frac{y^2 + [x(x + 2)]^2}{y^2 + [x(x - 2)]^2}$$

$$- \frac{y}{4x}\left(\tan^{-1}\frac{2x + x^2}{y} + \tan^{-1}\frac{2x - x^2}{y}\right) , \quad \text{(E5)}$$

where $x = K/k_F$ and $y = \Omega/\frac{1}{2}k_F^2$.

Numerical results for the correlation energy in various approximations are presented in Table IV and Fig. 5.

Table II shows a comparison of δE_{xc} as calculated in the LDA using the RPA, Hubbard,[23] Wigner,[24] and STLS[25] approximations. Note that at $r_s = 2$ the Wigner value is somewhat lower than the other values. This can be understood by inspection of Fig. 5. The LDA calculation of δE_{xc} samples the *difference* between $n\epsilon_{xc}(n)$ at the bulk density n and at the local density $n(\vec{x})$. This sampling is primarily toward lower densities (i.e., toward smaller values of k_F). The Wigner approximation for ϵ_{xc} vs k_F shows a somewhat flatter behavior at large k_F than do the other approximations, and so yields a smaller value of δE_{xc}.

An analytic parametrization of the RPA correlation energy has been given by von Barth and Hedin.[31] A comparable fit to the Hubbard correlation energy (for $k_F a_0 \leq 1$) can be obtained with the same functional form, but with $C^P = 0.0411$ Ry/electron. These parametrizations have been used in the self-consistent LDA calculations of Tables II and III. The other RPA and Hubbard calculations in this paper involve a numerical evaluation of (E1)–(E5).

[1]N. D. Lang and W. Kohn, Phys. Rev. B 1, 4555 (1970).
[2]P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964); W. Kohn and L. J. Sham, ibid. 140, A1133 (1965); N. D. Lang, Solid State Phys. 28, 225 (1973).
[3]J. Schmit and A. A. Lucas, Solid State Commun. 11, 415 (1972).
[4]R. A. Craig, Phys. Rev. B 6, 1134 (1972).
[5]P. J. Feibelman, Solid State Commun. 13, 319 (1973); W. Kohn, ibid. 13, 323 (1973).
[6]J. C. Phillips, Comments Solid State Phys. 6, 91 (1975); W. Kohn and N. D. Lang, ibid. 6, 95 (1975).
[7]V. Peuckert, Z. Phys. 241, 191 (1971); A. Griffin and

E. Zaremba, Phys. Rev. A 8, 486 (1973).
[8]J. Harris and R. O. Jones, J. Phys. F 4, 1170 (1974).
[9]E. Wikborg and J. E. Inglesfield, Solid State Commun. 16, 335 (1975).
[10]G. Srinivasan and M. Jonson, Solid State Commun. 15, 771 (1974); M. Jonson and G. Srinivasan, Phys. Scr. 10, 262 (1974); G. Srinivasan, M. Jonson, and S. Lundqvist, Nuovo Cimento B 29, 285 (1975).
[11]A. Griffin, H. Kranz, and J. Harris, J. Phys. F 4, 1744 (1974).
[12]N. D. Lang and L. J. Sham, Solid State Commun. 17, 581 (1975).
[13]D. C. Langreth and J. P. Perdew, Solid State Commun. 17, 1425 (1975).
[14]G. D. Mahan, Phys. Rev. B 12, 5585 (1975).

[15]In the bulk electron gas this "plasmon" contribution can be well defined within the RPA. It has been recently calculated for metallic densities (Ref. 11) and is about 20% of the magnitude of the total correlation energy.

[16]An alternate approach generalizing the LDA has recently been taken by J. S. Wang and M. Rasolt, Phys. Rev. B 13, 5330 (1976), who include the first gradient corrections to E_{xc} in a surface energy calculation. In a test against the soluble infinite-barrier model, they find that this approach is actually much less accurate than the LDA alone, but argue that the first gradient corrections may be more useful for the smoother density profiles of more realistic models.

[17]P. Nozières and D. Pines, Phys. Rev. 111, 442 (1958).

[18]O. Gunnarsson and B. I. Lundqvist, Phys. Rev. B 13, 4274 (1976).

[19]The techniques used in this section are quite similar to those used by D. M. Newns, Phys. Rev. B 1, 3304 (1970) in a different long-wavelength limit of the infinite-barrier model.

[20]It has been derived microscopically in the RPA by J. Harris and A. Griffin, Phys. Lett. A 34, 51 (1971), and by P. Feibelman, Phys. Rev. B 3, 220 (1971).

[21]J. I. Gersten, Phys. Rev. 188, 774 (1969); M. Šunjić and A. A. Lucas, Phys. Rev. B 3, 719 (1971); J. J. Chang and D. C. Langreth, Phys. Rev. B 5, 3512 (1972); B 8, 4638 (1973).

[22]D. Wagner, J. Phys. C 8, 1829 (1974); B. Gumhalter and D. M. Newns, Phys. Lett. A53, 137 (1975).

[23]J. Hubbard, Proc. R. Soc. Lond. 243, 336 (1957).

[24]E. P. Wigner, Phys. Rev. 46, 1002 (1934).

[25]K. S. Singwi, M. P. Tosi, R. H. Land, and A. Sjölander, Phys. Rev. 176, 589 (1968).

[26]D. Pines and P. Nozières, The Theory of Quantum Liquids (Benjamin, New York, 1966).

[27]J. P. Perdew, D. C. Langreth, and V. Sahni (to be published).

[28]J. P. Perdew and R. Monnier (to be published).

[29]Technically χ^{non} is not strictly the noninteracting susceptibility, because the propagators in Fig. 1(a) have self-energy corrections. In (D2) we need these only to first order in V, and hence the only formal effect on the equations that follow is that the single particle $\epsilon_{q\vec{k}}$ is different from that given by Eq. (D7).

[30]D. Pines, Elementary Excitations in Solids (Benjamin, New York, 1963), Appendix C.

[31]U. von Barth and L. Hedin, J. Phys. C 5, 1629 (1972).