Wave-vector analysis of metallic surface energy

Mark Rasolt
Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830
and University of Paris XI at Orsay, Orsay, France

G. Malmstrom and D. J. W. Geldart
Department of Physics, Dalhousie University, Halifax, Nova Scotia B3H 3J5, Canada
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The exchange and correlation energy of a nonuniform electronic system can be decomposed into contributions of different wave-vector fluctuations. Both the long- and short-wavelength contributions to this energy can be properly handled. A possible approach for the intermediate region is to interpolate between these two limits. We examine this interpolation scheme within the infinite-barrier model, as it applies to surface-energy calculations. Our study suggests that such schemes are inadequate for the treatment of this intermediate region.

I. INTRODUCTION

The exchange and correlation energy of a nonuniform fermion system in the presence of an external potential $V(r)$ is given by the well-known form[1]

$$E_{xc}=-\frac{1}{2}\int d^3r\int d^3r'\,v(\vec{r}-\vec{r}\,')\times\int_0^1 d\lambda\left(\int_0^\infty\frac{d\omega}{\pi}\chi_\lambda(\vec{r},\vec{r}\,',i\omega)+n_\lambda(\vec{r})\delta(\vec{r}-\vec{r}\,')\right), \tag{1}$$

where $\lambda v(\vec{r}-\vec{r}\,')$ is some arbitrary particle-particle interaction of coupling strength λ, $\chi_\lambda(\vec{r},\vec{r}\,',i\omega)$ is the response function of the system, and $n_\lambda(\vec{r})$ is the corresponding density. Making the connection with the structure factor $S(\vec{r},\vec{r}\,')$

$$NS_\lambda(\vec{r},\vec{r}\,')=-\int_0^\infty\frac{d\omega}{\pi}\chi_\lambda(\vec{r},\vec{r}\,',i\omega) \tag{2}$$

(where N is the number of particles), E_{xc} is then given by

$$E_{xc}=+\frac{1}{2}\int d^3r\int d^3r'\,v(\vec{r}-\vec{r}\,')\times\int_0^1 d\lambda[NS_\lambda(\vec{r},\vec{r}\,')-n_\lambda(\vec{r})\delta(\vec{r}-\vec{r}\,')]. \tag{3}$$

Equation (3) can be transformed and written

$$E_{xc}\equiv N\int\frac{d^3q}{(2\pi)^3}E_{xc}(\vec{q})=\frac{N}{2}\int\frac{d^3q}{(2\pi)^3}v(q)\int_0^1 d\lambda[S_\lambda(\vec{q},\vec{q})-1], \tag{4}$$

with

$$S_\lambda(\vec{q},\vec{q})\equiv\int d^3r\int d^3r'\,e^{-i\vec{q}\cdot\vec{r}}e^{+i\vec{q}\cdot\vec{r}'}S_\lambda(\vec{r},\vec{r}\,'). \tag{5}$$

Equation (4) is *exact* but its evaluation for an arbitrary nonuniform fermion system is presently a virtually impossible task. An approximation for Eq. (4) has been suggested by Hohenberg and Kohn[2] (HK) and is referred to as the local-density approximation (LDA). In the LDA, Eq. (4) is approximated by

$$E_{xc}\approx E_{xc}^{\mathrm{LD}}=\int d^3r\,n(\vec{r})\epsilon_{xc}(n(\vec{r})), \tag{6}$$

where $\epsilon_{xc}(n(\vec{r}))$ is the exchange-correlation energy per electron of a homogeneous electron gas of density $n(\vec{r})$. A connection between Eqs. (4) and (6) can be made if Eq. (6) is also decomposed in terms of its wave-vector components. Then

$$E_{xc}^{\mathrm{LD}}=\frac{1}{2}\int\frac{d^3q}{(2\pi)^3}\int d^3r\int_0^1 d\lambda\,v(\vec{q})n(\vec{r})\times[S_\lambda^h(\vec{q},n(\vec{r}))-1], \tag{7}$$

where $S_\lambda^h(\vec{q},n(\vec{r}))$ is the structure factor of the homogeneous electron gas with local density $n(\vec{r})$.

In the limit of large-wave-vector fluctuations (large $\vec{q}$), Eq. (4) reduces to Eq. (7).[3] As the wave vector of the fluctuation gets smaller, this agreement is expected to worsen. To correct for this intermediate range of $\vec{q}$, HK have suggested adding a nonlocal correction E_{xc}^{nl} (to the exchange and correlation energy) of the form[2]

$$E_{xc}^{\mathrm{nl}}\approx-\frac{1}{4}\int d^3r\int d^3r'\,K_{xc}(\vec{r}-\vec{r}\,',n(\vec{r}_0))\times[n(\vec{r})-n(\vec{r}\,')]^2, \tag{8}$$

where K_{xc} is expressed in terms of the dielectric function for the homogeneous electron gas.[2]

So far our discussion has been general enough to emcompass the exchange and correlation energy of any nonuniform fermion system. We now focus

our attention to a nonuniform electron system as given by a surface of a metal. We further restrict our discussion to the surface energy; i.e., the energy (per unit area) required to cleave this nonuniform electron gas in two.[4]

In the exact formulation [Eq. (3)], the calculation of the surface energy would involve extracting the contribution to E_{xc} which is proportional to the cleaved surface area[5] (see also Sec. II). In the LDA it would involve introducing the appropriate density for the uncleaved and cleaved systems in Eq. (6) or (7) and evaluating their difference. We expect the LDA to misrepresent the full surface energy mostly in the intermediate- and small-$\vec{q}$ limits. However, in the case of the E_{xc} contribution to the surface energy the limit of small wave vectors is also known exactly.[3] A thorough discussion of this limit is given in Ref. 3 where the proper spherical average required in calculating the small $|\vec{q}| \equiv q$ limit of Eq. (4) is emphasized. Such careful averaging is important since the $q \to 0$ limit differs according to whether $\vec{q}$ is parallel to the surface ($q_\parallel$) or perpendicular to it (q_z). Since *all* small-$\vec{q}$ fluctuations are unlikely to be accurately treated in the LDA the average of both $q_\parallel$ and q_z must be included in the small-$\vec{q}$ form of E_{xc}.

After a lengthy analysis the contribution to the surface energy of Eq. (4) at small q are derived and given in Ref. 3 as

$$\frac{E_{xc}}{2A} = \int \frac{dq}{k_F}\gamma(q)\,, \tag{9}$$

with the small-q limit given by

$$\lim_{q\to 0}\gamma(q) = (k_F/8\pi)q(\omega_s - \tfrac{1}{2}\omega_p) \tag{10}$$

where k_F is given in terms of the bulk density n_0 by $k_F = (3\pi^2 n_0)^{1/3}$. A is the area of the cleaved surface and ω_p and ω_s are the bulk- and surface-plasmon frequencies, respectively (i.e., $\omega_s = \omega_p/\sqrt{2}$).

Two features of Eq. (10) are of particular interest. First the $q \to 0$ limit has a universal structure independent of surface details. Second its form contains explicitly surface-plasmon contributions; contributions which are not at all likely to be accounted for by LDA or any additional corrections of a bulk form [Eq. (8)].[2] Since both the large- and small-q limits are known exactly [the former given by Eq. (7) and the latter by Eq. (10)], the following procedure has been suggested[3] in treating the *full* E_{xc}. Use the LDA [by introducing the appropriate density in Eq. (7)] to construct $\gamma(q)$ for large q and use Eq. (10) for evaluating $\gamma(q)$ in the small-q limit. To determine the unknown intermediate range of q interpolate between the two. For example, in the infinite-barrier model (IBM), where the total exchange and correlation contribution are known,[1,5] this wave-vector-interpolation (WVI) procedure results in $\gamma(q)$ given in Fig. 1. The solid curve represents $\gamma(q)$ as obtained from Eq. (7) using the density

$$n(z) = n_0[1 + (3/y^3)(y\cos y - \sin y)]\,, \tag{11}$$

with $y = 2k_F z$. The dash-dotted line is $\gamma(q)$ given by Eq. (10). The dashed arc is the arc of a circle which is tangent to the straight line at $q = 0$ and to $\gamma_{\mathrm{LD}}(q)$ at some larger value of q around the peak (located at q approximately k_F) value of $\gamma_{\mathrm{LD}}(q)$. The area between the dashed and solid curves is the correction for the LDA in the intermediate region of q and is found to account accurately for the full IBM E_{xc} when *integrated*.

Two points are worth emphasizing in Fig. 1. First since this procedure accounts for the numerical value of the *full* E_{xc} then in addition to the surface-plasmon contribution the shaded area must also have accounted for the very complicated K_{xc} term of Eq. (8). Second there seems to be an implicit assumption that for $q > k_F$ nonlocal corrections to the LDA can be ignored since the WVI corrects the LDA only for $q \lesssim k_F$. It is precisely these points that we wish to investigate in this work. We will show that $\gamma(q)$ contains too much structure (in the intermediate region of q) for

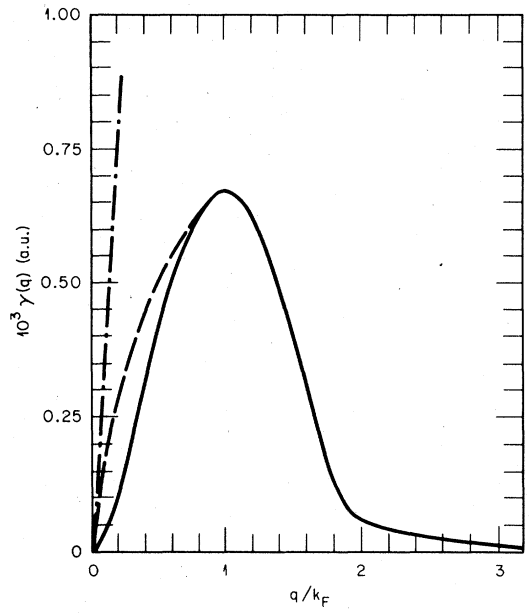

FIG. 1. Wave-vector decomposition of the exchange and correlation contribution to the surface energy of the IBM in the RPA for $r_s = 2.07$ (taken from Ref. 3). Solid curve is the LDA, dash-dotted line from Eq. (9) and dashed curve the interpolation.

such a simple interpolation scheme to be meaningful.

In Sec. II we spherically decompose the exchange contribution to the surface energy of the IBM following strictly the above discussion. In Sec. III we numerically evaluate the exchange surface contribution from $q=0$ to $3k_F$ to exhibit its structure. In Sec. IV conclusions are drawn concerning the validity of the above WVI procedure.

An accurate description for the exchange and correlation contribution of and inhomogeneous electron gas has both fundamental and practical importance. While individually these terms are small in comparison with the kinetic and electrostatic contributions, due to large cancellations that occur in many calculations (surface energy being one example) these terms end up comprising a very large contribution. The simplicity with which the WVI procedure is intended to account for these contributions has given it a wide appeal. While it does suggest a systematic way for incorporating the surface plasmons contribution into E_{xc}, its detailed accuracy has not been carefully scrutinized for finite q and thus should be further examined and improved. Such studies are presently in progress and, in the following, we report results for the exchange contribution.

II. WAVE-VECTOR DECOMPOSITION OF THE EXCHANGE SURFACE ENERGY IN THE IBM

Consider the problem of N electrons in the presence of an external potential $V(\vec{r})$. The wave function of an electron of energy ϵ_i is given by

$$\left(-\frac{\hbar^2}{2m}\nabla^2+V(\vec{r})\right)\phi_i(\vec{r})=\epsilon_i\phi_i(\vec{r})\,. \tag{12}$$

Similar to Refs. 1, 3, and 5 we will not consider the question of self-consistency. Then the coupling constant integration in Eq. (1) can be easily performed to yield the well-known form for the exchange energy[1]

$$E_x=-\frac{1}{4}\int d^3r\int d^3r'\,v(\vec{r}-\vec{r}\,')\,|\rho(\vec{r},\vec{r}\,')|^2\,, \tag{13}$$

where

$$\rho(\vec{r},\vec{r}\,')=2\sum_i\phi_i(\vec{r})\phi_i^*(\vec{r}\,')\theta^<(\epsilon_i-\epsilon_F)\,. \tag{14}$$

The index i covers the occupied states and $\epsilon_F=\hbar^2k_F^2/2m$ is the Fermi energy.

$$\Theta^>(x)=\begin{cases}1, & x>0,\\ 0, & x<0,\end{cases}\qquad \Theta^<(x)=1-\Theta^>(x)\,.$$

Equation (13) can be decomposed into its wave-vector components to yield

$$E_x=\frac{N}{2}\int\frac{d^3q}{(2\pi)^3}v(\vec{q})[S^x(\vec{q},\vec{q})-1]\,, \tag{15}$$

where

$$N[S^x(\vec{q},\vec{q})-1]=-\frac{1}{2}\int d^3r\int d^3r'\,e^{i\vec{q}\cdot(\vec{r}-\vec{r}')}\,|\rho(\vec{r},\vec{r}\,')|^2\,. \tag{16}$$

If we choose the IBM,[1] then $\phi_i(\vec{r})$ of Eq. (12) is given by

$$\phi_i(\vec{r})=[2/(L+\delta)]^{1/2}\sin(k_zz)e^{i\vec{k}\cdot\vec{x}}\,, \tag{17}$$

where $k_z=n\pi/(L+\delta)$ (with $n=1,\ldots,\infty$) and $\vec{k}$ and $\vec{x}$ are two-dimensional vectors perpendicular to the z axis. L and δ are given in the Appendix and are the length of the uniform density set at $\frac{1}{2}\delta$ from the infinite potential barrier.

Using Eq. (17) in Eqs. (15) and (16) the following form is readily derived:

$$E_x=-\frac{A}{(2\pi)^2}\int\frac{d^3q}{(2\pi)^3}v(\vec{q})\sum_{k_z,k_z'}H(q_{\parallel},k_z,k_z')\times F(q_z,k_z,k_z')\,, \tag{18}$$

where

$$H(q_{\parallel},k_z,k_z')=\int d^2k'\int d^2k\,\delta(\vec{q}_{\parallel}+\vec{k}'-\vec{k})\Theta^>(k_F^2-k_z^2-k^2)\times\Theta^>(k_F^2-k_z'^2-k'^2)\,, \tag{19}$$

$$F(q_z,k_z,k_z')=\lim_{\Delta\to0}\int_0^{L+\delta}dz\int_0^{L+\delta}dz'\,e^{-\Delta|z-z'|}f(z')e^{-iq_zz'}\times f(z)e^{+iq_zz}\,, \tag{20}$$

and

$$f(z)=[2/(L+\delta)]\sin k_zz\,\sin k_z'z\,. \tag{21}$$

We note that in the above form the wave-vector decomposition requires that the interparticle interaction of component $\vec{q}$ be written

$$v(\vec{r}-\vec{r}\,')=\lim_{\Delta\to0}v(q)e^{i\vec{q}\cdot(\vec{r}-\vec{r}')}e^{-\Delta|z-z'|}\,. \tag{22}$$

After some lengthy analysis we get the following form for E_x:

$$E_x=\frac{-A}{32\pi^5}\int d^3q\,v(q)\left[\frac{\pi}{L+\delta}[\Gamma_1(q_{\parallel},q_z)+\Gamma_2(q_{\parallel},q_z)]+\left(\frac{\pi}{L+\delta}\right)^2\left(\frac{\Gamma_3(q_{\parallel},q_z)}{\pi^2}+\frac{\Gamma_4(q_{\parallel},q_z)}{\pi^2}\right)\right]\,, \tag{23}$$

where

$$\Gamma_1(q_\parallel,q_z) = \sum_{k_z,k_z'} H(q_\parallel,k_z,k_z')[\delta(q_z-k_-)+\delta(q_z+k_+)], \tag{24}$$

$$\Gamma_2(q_\parallel,q_z) = \sum_{k_z} H(q_\parallel,k_z,k_z)\delta(q_z), \tag{25}$$

$$\Gamma_3(q_\parallel,q_z) = \lim_{\Delta\to 0}\sum_{k_z,k_z'} H(q_\parallel,k_z,k_z')\,\mathrm{Re}\left(\frac{1}{(q_z-k_--i\Delta)^2}+\frac{1}{(q_z-k_+-i\Delta)^2}\right), \tag{26}$$

and

$$\Gamma_4(q_\parallel,q_z) = \mathcal{P}\sum_{k_z,k_z'} H(q_\parallel,k_z,k_z')\times\left[\left(-\frac{2}{k_++k_-}-\frac{2}{k_--k_+}+\frac{1}{k_-}\right)\frac{1}{(q_z-k_-)}+\left(-\frac{2}{k_++k_-}+\frac{2}{k_--k_+}+\frac{1}{k_+}\right)\frac{1}{q_z-k_+}\right]. \tag{27}$$

$k_-=k_z-k_z'$, $k_+=k_z+k_z'$, $\mathcal{P}$ in Eq. (27) stands for the principal part, and $H(q_\parallel,k_z,k_z')$ is given in Eq. (19).

Our next task is to extract the surface energy terms from Eqs. (23)–(27); i.e., terms proportional to A. This is straightforward and involves simply a careful application of the Euler-Maclaurin formula.[6] We write below the final results:

$$E_x = -\frac{A}{32\pi^6}\int d^3q\, v(q)[(L+\delta)\Gamma_1'(q_\parallel,q_z)+\Gamma_2'(q_\parallel,q_z)+\Gamma_3'(q_\parallel,q_z)+\Gamma_4'(q_\parallel,q_z)], \tag{28}$$

where

$$\Gamma_1'(q_\parallel,q_z) = \int_0^\infty dk_z\int_0^\infty dk_z' H(q_\parallel,k_z,k_z')\times[\delta(q_z-k_-)+\delta(q_z-k_+)] - \frac{2\pi}{L+\delta}\int_0^\infty dk_z H(q_\parallel,0,k_z)\delta(q_z+k_z), \tag{29}$$

$$\Gamma_2'(q_\parallel,q_z) = \pi\int_0^\infty dk_z H(q_\parallel,k_z,k_z)\delta(q_z), \tag{30}$$

$$\Gamma_3'(q_\parallel,q_z) = \lim_{\Delta\to 0}\frac{1}{\pi}\int_0^\infty dk_z\int_0^\infty dk_z' H(q_\parallel,k_z,k_z')\times\mathrm{Re}\left(\frac{1}{(q_z-k_--i\Delta)^2}+\frac{1}{(q_z-k_+-i\Delta)^2}\right), \tag{31}$$

$$\Gamma_4'(q_\parallel,q_z) = \frac{1}{\pi}\mathcal{P}\int_0^\infty dk_z\int_0^\infty dk_z' H(q_\parallel,k_z,k_z')\left[\left(-\frac{2}{k_++k_-}-\frac{2}{k_--k_+}+\frac{1}{k_-}\right)\frac{1}{q_z-k_-}+\left(-\frac{2}{k_++k_-}+\frac{2}{k_--k_+}+\frac{1}{k_+}\right)\frac{1}{q_z-k_+}\right], \tag{32}$$

where the primes in Eqs. (29)–(32) indicate that these terms individually originated in the unprimed terms of Eqs. (24)–(27).

The last three terms in Eq. (28) are proportional to A. The first term has a contribution proportional to the volume V which is subtracted out when we evaluate the surface energy (see the Appendix) leaving

$$(L+\delta)\Gamma_1'(q_\parallel,q_z) = \delta\left(\int_0^\infty dk_z\int_0^\infty dk_z' H(q_\parallel,k_z,k_z')[\delta(q_z-k_-)+\delta(q_z-k_+)]\right) - \int_0^\infty dk_z H(q_\parallel,0,k_z)\delta(q_z+k_z). \tag{33}$$

We note that the term in Eq. (33) multiplying δ is simply the exchange energy of a bulk electron per unit volume.[1,5]

Our final task is to produce a form for $\gamma(q)$ [Eq. (9)] in the IBM for the exchange approximation. This involves replacing $|q_\parallel|$ and q_z' by its spherical coordinate form (i.e., $|q_\parallel|=q\sin\theta$; $q_z=q\cos\theta$) and integrating Eq. (28) over the solid angle.

With $x\equiv\cos\theta$, we get

$$\frac{E_x}{2A}\equiv\int\frac{dq}{k_F}\gamma(q) = \int\frac{dq}{k_F}v(q)k_F\left(\int dk_z\int dk_z'\frac{q^2}{32\pi^6}\int_{-1}^{+1}dx\,H(q,x,k_z,k_z')[\phi(q,x,k_-,k_+)+\phi(q,x,k_+,k_-)] + \frac{1}{16\pi^4}q\int dk_z\,\psi(q,k_z)+\delta n_0\frac{q^2}{8\pi^2}[S_x^h(q,n_0)-1]\right), \tag{34}$$

where

$$\phi(q,x,k_-,k_+) = -\lim_{\Delta\to 0}\mathrm{Re}\frac{1}{(qx-k_- - i\Delta)^2} - \mathcal{P}\left(\frac{1}{k_-}-\frac{2}{k_++k_-}-\frac{2}{k_--k_+}\right)\frac{1}{qx-k_-} \tag{35}$$

and

$$\psi(q,k_z) = H(q,(1-k_z^2/q^2)^{1/2},0,k_z)\Theta^>(q^2-k_z^2) - \tfrac{1}{2}H(q,0,k_z,k_z)\,. \tag{36}$$

The last term in Eq. (34) corresponds to the bulk contribution, in the exchange, per unit volume multiplied by the length $\delta = 3\pi/4k_F$ (the Appendix). The bulk contribution is well known and is given by[7]

$$S_x^h(q,n_0) - 1 = \tfrac{1}{2}\Theta^>(2k_F-q)\left(-2+\frac{3}{2}\frac{q}{k_F}-\frac{1}{8}\frac{q^3}{k_F^3}\right). \tag{37}$$

The explicit structure of $H(q,x,k_z,k_z')$ is easily evaluated from Eq. (19) and for completeness we write its form below:

$$H(q,x,k_z,k_z') = \Theta^<(k_z-k_F)\Theta^<(k_z'-k_F)(\pi(k_F^2-k_z'^2)\Theta^>(a_1-q(1-x^2)^{1/2})+\pi(k_F^2-k_z^2)\Theta^>(-a_1-q(1-x^2)^{1/2}) + \Theta^<(q(1-x^2)^{1/2}-a_0)\Theta^<(|a_1|-q(1-x^2)^{1/2}) \times\{\cos^{-1}(\omega_1)(k_F^2-k_z'^2)+\cos^{-1}(\omega_2)(k_F^2-k_z^2)-[(1-x^2)(k_F^2-k_z^2)(1-\omega_2^2)]^{1/2}q\}), \tag{38}$$

where

$$a_0 = (k_F^2-k_z^2)^{1/2}+(k_F^2-k_z'^2)^{1/2}, \tag{39a}$$

$$a_1 = (k_F^2-k_z^2)^{1/2}-(k_F^2-k_z'^2)^{1/2}, \tag{39b}$$

$$\omega_1 = \frac{k_z^2-k_z'^2+(1-x^2)q^2}{2q[(1-x^2)(k_F^2-k_z'^2)]^{1/2}}, \tag{39c}$$

$$\omega_2 = \frac{k_z'^2-k_z^2+(1-x^2)q^2}{2q[(1-x^2)(k_F^2-k_z^2)]^{1/2}}. \tag{39d}$$

Equations (34)-(37) are the first explicit forms for $\gamma(q)$ derived for *any* spherical interparticle interaction in the IBM. In the Sec. III, we numerically evaluate $\gamma(q)$ for bare Coulomb and Yukawa interparticle interactions and for a range of q. In Sec. IV we draw conclusions about the merit of the WVI method and suggest possible improvements.

III. NUMERICAL RESULTS

To evaluate Eq. (34) for a range of q is now relatively straightforward. The one-dimensional integral [last term in Eq. (34)] poses no difficulty. To evaluate the three-dimensional contribution ($E_x^{3\text{-D}}$) we integrate by parts. Using the structure of $H(q,x,k_z,k_z')$ we get after a lengthy calculation

$$\frac{E_x^{3\text{-D}}}{2A} = \frac{1}{32\pi^6}\int_0^\infty dq\,qv(q)\int_0^\infty dk_z\int_0^\infty dk_z'\left(\mathcal{P}\int_{-1}^{+1}dx\,H'(q,x,k_z,k_z')\,[\phi'(q,x,k_-,k_+)+\phi'(q,x,k_+,k_-)] + \sigma(q,k_+,k_-)+\sigma(q,k_-,k_+)\right), \tag{40}$$

where

$$\phi'(q,x,k_+,k_-) = -\frac{1}{qx-k_-}-\left(\frac{2}{k_++k_-}+\frac{2}{k_--k_+}-\frac{1}{k_-}\right)\ln|qx-k_-|\,, \tag{41a}$$

$$\sigma(q,k_+,k_-) = \frac{1}{q-k_-}+\frac{1}{q+k_-}+2\left(\frac{1}{k_++k_-}+\frac{1}{k_--k_+}-\frac{1}{2k_-}\right)\ln\left|\frac{q-k_-}{q+k_-}\right|, \tag{41b}$$

and

$$H'(q,x,k_z,k_z') = \Theta^<(q(1-x^2)^{1/2}-a_0)\Theta^<(|a_1|-q(1-x^2)^{1/2})\left[\frac{q^2x}{x^2-1}(B_2-x^2)^{1/2}(x^2-B_1)^{1/2}\right], \tag{41c}$$

with $B_1 = 1-a_0^2/q^2$ and $B_2 = 1-a_1^2/q^2$.

Again in Eq. (40) the two-dimensional integral (over k_z and k_z') poses little problem and the numerical integral requiring some care is the remaining three dimensional integral of Eq. (40). This integral can be written

$$\frac{E'^{3\text{-D}}}{2A} = \frac{1}{32\pi^6}\int_0^\infty dq\,qv(q)\int_0^{k_F}dk_z'\int_0^{k_F}dk_z\,\mathcal{P}\int_{\beta_1}^{\beta_2}dx\left(\frac{q^2x}{x^2-1}(B_2-x^2)^{1/2}(x^2-B_1)^{1/2}\right) \times\sum_\pm\left[\frac{2x}{q}\frac{1}{x^2-k_\pm^2/q^2}+\left(\frac{1}{k_z}\pm\frac{1}{k_z'}-\frac{1}{k_\pm}\right)\ln\left(\frac{|x-k_\pm/q|}{x+k_\pm/q}\right)\right], \tag{42}$$

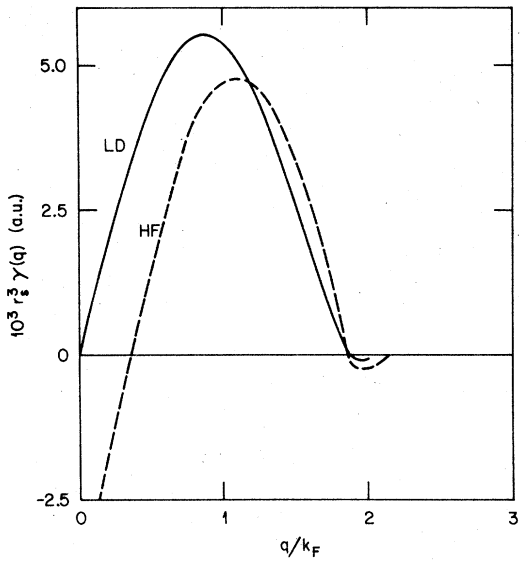

FIG. 2. Wave-vector decomposition of exchange contribution to the surface energy of the IBM with bare Coulomb interparticle interaction. Solid curve (labeled LD) is the LDA [Eq. (44)], dashed curve [labeled HF (Hartree-Fock)] is the full exchange [Eq. (34)].

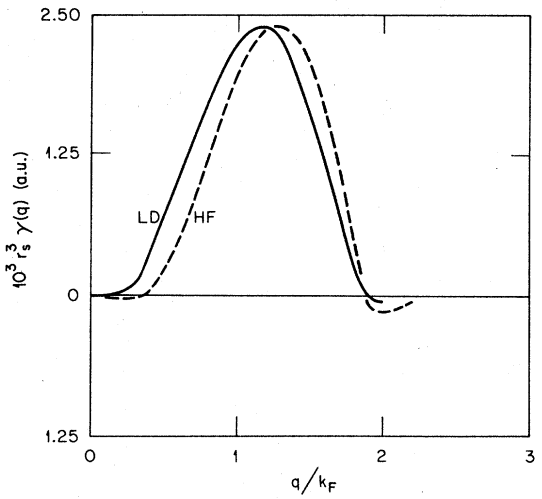

FIG. 3. Same as Fig. 2 with a Yukawa interparticle interaction $4\pi e^2/(q^2+\lambda^2)$. The screening length λ is set equal to the Thomas-Fermi screening length and the density is $r_s=2$.

in which the limits of the principle-part x integration are $\beta_1=\mathrm{Re}\sqrt{B_1}$ and $\beta_2=\mathrm{Re}\sqrt{B_2}$ with $0\leq\beta_1\leq\beta_2\leq 1$. The numerical problems arise because for certain values of the parameters, the point singularity of the innermost x singularities can be arbitrarily close, thus rendering unreliable simple-minded methods for evaluation of the required principle-part integral. (In fact, even after integration over x, the k_z, k_z' integration has a singularity; however, this local singularity can be removed by a transformation into polar coordinates.) In order to obtain sufficient accuracy, we found it necessary to adopt the following procedure. Denoting the x integrand by $g(x)$, a function of the complex variable z was constructed such that $\mathrm{Re}g(z=x+i0^+)=g(x)$ for $\beta_1<x<\beta_2$; $g(z)$ is analytic in the upper half of the z plane. $\mathrm{Re}g(z=x+i0^+)$ generates δ functions for $0\leq x\leq\beta_1$ and for $\beta_2\leq x<\beta_3$, so that the first and third integral in

$$\mathrm{Re}\left(\int_0^{\beta_1} dx\, g(x+i0^+)+\int_{\beta_1}^{\beta_2} dx\, g(x+i0^+)+\int_{\beta_2}^{\beta_3} dx\, g(x+i0^+)-\int_\Gamma dz\, g(z)\right)=0 \tag{43}$$

can be evaluated analytically. The path of integration Γ in the fourth integral begins at $z=0$ and ends at $z=\beta_3$ (which is real and can be chosen as found convenient) and lies in the upper-half plane well removed from singularities of $g(z)$. Consequently, the fourth integral can be evaluated numerically without difficulty to give an accurate result for the original principal-value integral, the second term in Eq. (43).

In Fig. 2 we display $\gamma(q)$ as a function of q when $v(q)$ is the bare Coulomb interaction, $4\pi e^2/q^2$. In Fig. 3 we plot $\gamma(q)$ for a Yukawa interparticle interaction $v(q)=4\pi e^2/(q^2+\lambda^2)$ with the inverse Thomas-Fermi screening length evaluated at a density corresponding to $r_s=2$. In addition to the full exchange, we also include in Figs. 2 and 3 the equivalent local density $\gamma_{\mathrm{LD}}(q)$ calculated from Eqs. (7) and (37) which gives

$$\int\frac{dq}{k_F}\gamma_{\mathrm{LD}}(q)=\int\frac{dq}{k_F}v(q)\frac{q^2k_F}{4\pi^2}\int d^3r\, n(\vec{r})\left\{\Theta(2k_F(\vec{r})-q)\left[-2+\frac{3}{2}\frac{q}{k_F(\vec{r})}-\frac{1}{8}\left(\frac{q}{k_F(\vec{r})}\right)^3\right]-\Theta(2k_F-q)\right.$$
$$\left.\times\left[-2+\frac{3}{2}\frac{q}{k_F}-\frac{1}{8}\left(\frac{q}{k_F}\right)^3\right]\right\}, \tag{44}$$

with $k_F(\vec{r})=[3\pi^2 n(\vec{r})]^{1/3}$, k_F the uniform Fermi momentum $[k_F=(3\pi^2 n_0)^{1/3}]$, and $n(\vec{r})$ given in Eq. (11). In Sec. IV we discuss the implications of these results.

IV. DISCUSSION AND CONCLUSION

The most striking feature of the results presented in Figs. 2 and 3 is the sizable lack of

agreement between $\gamma(q)$ and $\gamma_{LD}(q)$ for q much beyond the peak (i.e., $q > k_F$). Even for $q > 2k_F$ there remains contributions in $\gamma(q)$ that is not part of $\gamma_{LD}(q)$. Of course some of the discrepancy (but not all, particularly not for $q > 2k_F$) would be removed by the inclusion of correlation (see below). The WVI method presented in Sec. I (Fig. 1) could not possibly account for this difference between the local density and full exchange. Another interesting observation can be drawn from Fig. 3. In Fig. 3 λ was chosen to be large enough so that the full and LDA exchange surface energy are in good agreement (Fig. 5, Ref. 8). However, from Fig. 3, we see that for individual wave vectors q there nevertheless exists considerable difference between $\gamma(q)$ and $\gamma_{LD}(q)$. The net agreement in the integrated areas is clearly a consequence of cancellations between $q < k_F$ and $q > k_F$ regions. This questions the assumption that if the total surface energy is in good agreement then each individual q contribution to $\gamma_{LD}(q)$ and $\gamma(q)$ carries similar agreement. Such an assumption is made for example in the treatment of the IBM when correlation is included by the WVI method.

To carry out the q-vector decomposition of the IBM, when correlations are included, is an extremely difficult task. However, our results in the exchange approximation allow us to draw some interesting conclusions concerning the effect of correlations. For example if we turn to a high-density system in which the correlation contribution to $\gamma(q)$ and $\gamma_{LD}(q)$, for a *finite-q* value, is of the order[9] e^4 (e^2 being the first power of the interparticle interaction) and for which the exchange contribution to $\gamma(q)$ and $\gamma_{LD}(q)$ is of the order of e^2, then the difference in Fig. 2 (particularly for $q > k_F$) cannot possibly be totally corrected by correlation. This does not apply to the limit of small q, of course. Fixing e^2 at a finite value and then taking the limit of $q \to 0$ gives for $\gamma(q)$ the form in Eq. (10), which goes to zero at $q = 0$. From the small-q behavior of $\gamma(q)$ in the exchange approximation (Fig. 2) it is clear that correlation will introduce a major cancellation in this q going to zero limit. Similar delicate cancellation, at small q, occurs in the bulk exchange and correlation structure of $E_{xc}^{LD}(q)$. If we neglect the contribution from the (-1) in Eq. (7) (a term proportional to the density and therefore irrelevant to the surface energy) we find the well-known limits[9]

$$\lim_{q\to 0} E_x(q) = \frac{3\pi e^2}{2qk_F}, \quad \lim_{q\to 0} E_c(q) = -\frac{3\pi e^2}{2qk_F} + \frac{\omega_p}{2}. \quad (45)$$

This cancellation cannot persist for finite q, where $E_c(q)$ is of the order of e^4. We also note that the small-q region must poses considerable variation since the integration over the small-q region yields an $e^4 \ln e^2$ behavior.[10] Furthermore it should be emphasized (see Figs. 2 and 3) that there is considerable variation in $\gamma(q) - \gamma_{LD}(q)$ even for q of the order of $2k_F$, a variation which changes sign twice in the range of $q = 0$ to $3k_F$. In view of the above comments concerning the different charge dependence of exchange and correlation it is highly speculative (and certainly not demonstrated) that correlation could precisely restore agreement with the local-density approximation as implied by the WVI.

The structure of K_{xc} in Eq. (8) has also been studied from electron-gas considerations.[11-15] As stressed in the Introduction such a structure is unlikely to include surface-geometry effects, such as surface plasmons. It thus remains a basic problem of how to include these contributions into K_{xc}. A possible approach is to combine the high-q structure of K_{xc} with Eq. (10) using similar procedures suggested in Refs. 3, 16, and 17. It is, however, essential to first demonstrate (within a model calculation) to what accuracy does the inclusion of K_{xc} account for the large difference in the intermediate-q region. Such work is in progress.

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APPENDIX

In this appendix we wish to define the surface energy within the IBM in some detail.

Consider N electrons inside a box of length $L + \delta$ bounded at $z = 0$ and $z = L + \delta$ by an infinite potential barrier (Fig. 4); this is the IBM. The sur-

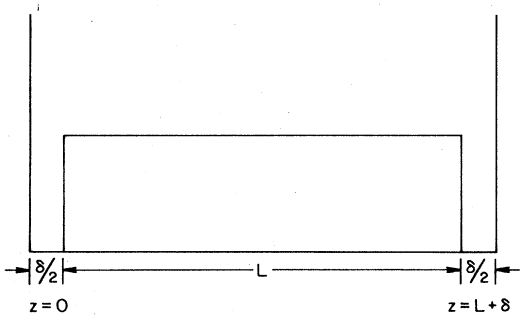

FIG. 4. IBM with the edge of the uniform density set at $\frac{1}{2}\delta$ from the infinite potential barrier.

face energy is defined as the difference between the IBM configuration and the configuration where the electrons are uniformly distributed in the volume $V = LA$ with density $n_0 = k_F{}^3/3\pi^2 = N/V$. The value of δ is determined from the following conditions: (a) the number of electrons in $A(L+\delta)$ is N and (b) the density for large z, is to order $1/L$, n_0. Now since the eigenvalues are $k_z = m\pi/(L+\delta)$

$$N = \frac{A}{\pi}\sum_{m=1}^{M} k_\nu^2 - \left(\frac{m\pi}{L+\delta}\right)^2, \tag{A1}$$

where the occupied states lie within a hemisphere of radius k_ν.[18] Applying the Euler-Maclaurin for formula[6] to (A1), we get to order $1/L$:

$$N = \frac{AL}{3\pi^2}k_\nu^3 + \frac{A\delta}{3\pi^2}k_\nu^3 - \frac{A}{4\pi}k_\nu^2. \tag{A2}$$

Now the density $n(z)$ is given by

$$n(z) = \frac{4}{L+\delta}\sum_{m=0}^{M}\left[k_\nu^2 - \left(\frac{m\pi}{L+\delta}\right)^2\right]\left[\sin\left(\frac{m\pi z}{L+\delta}\right)\right]^2, \tag{A3}$$

which goes to n_0 for large z if k_ν is chosen to be equal to k_F. Setting $k_\nu = k_F$ in (A2) yields $\delta = 3\pi/4k_F$.

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