Gradient Corrections in the Exchange and Correlation Energy of an Inhomogeneous Electron Gas*

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An exact result is derived for the coefficient B_{xc} which determines the first gradient corrections to the exchange and correlation energy of an inhomogeneous electron gas. A method of approximation, which is based on the random-phase approximation and is exact at high density, is given for the explicit evaluation of B_{xc}. Numerical results are also given for the metallic density range and applications are discussed.

Hohenberg, Kohn, and Sham[1-3] suggested the following gradient expansion for the exchange and correlation energy of an electron gas of slowly varying density:

$$E_{xc}(n) = \int d^3r \left\{ A_{xc}(n(\vec{r})) + B_{xc}(n(\vec{r})) [\nabla n(\vec{r})]^2 + \ldots \right\}.$$

(1)

This expansion has been applied to a wide variety of problems including surface physics,[4-7] electron-hole droplets,[8-10] cohesive energy of solids, etc. Although A_{xc} is reasonably well known at matallic densities, B_{xc} is not and various approximations have been introduced.[11-13] There has even been confusion about the correct sign of B_{xc}. Recently, the exchange contributions to B_{xc} have been calculated to all orders in e^2 in a self-consistent Hartree-Fock approximation.[14-16] In this case of bare Coulomb interactions, it was shown that the gradient expansion [Eq. (1)] does not even exist. Clearly, there is a need for a reliable calculation of B_{xc} which consistently includes *both* exchange and correlation at metallic densities.

In this Letter, we report the following results. (1) A closed-form expression for B_{xc} is given which includes all exchange and correlation effects exactly to all orders in e^2. (2) This exact but formal expression for B_{xc} is evaluated in an approximation which (a) includes the high-density limit and the lowest-order random phase–approximation (RPA) effects exactly, (b) incorporates

remaining higher-order contributions in an average way in the spirit of Hubbard,[17] and (c) is consistent with the Ward identities and the compressibility sum rule.[11] (3) Numerical results are given for B_{xc} in the metallic density range. Some results of their application to the problem of surface energies are also given. (4) Finally, we discuss some features of correlation effects which are important to bear in mind when comparing B_{xc} for atoms[13] and metallic systems.

The gradient coefficient in Eq. (1) is related to the long-wavelength expansion[1,11] of the screening function, $F(k) = a^{-1} + b\vec{k}^2 + \ldots$, by[18]

$$B_{xc} = (a^2 b - a_0^2 b_0)/2,$$

(2)

where $a = -d\mu/dn$ and a_0 and b_0 denote the corresponding expansion coefficients for noninteracting electrons. To evaluate b, we require the expansion to order $\vec{k}^2$ of

$$F(\vec{k}) = 2\,\mathrm{tr}_p G(p - \vec{k}/2) G(p + \vec{k}/2) \Lambda_p(\vec{k}),$$

(3)

where G and Λ denote the exact electron propagator and the vertex function, respectively, and $\mathrm{tr}_p \equiv [(2\pi)^4 i]^{-1} \int d^4p$. In a convenient matrix notation, the integral equation satisfied by the vertex function is $\Lambda = 1 + \gamma R \Lambda$, where $R = G(p - \vec{k}/2) G(p + \vec{k}/2)$ and γ is the irreducible scattering function. R and γ can be expanded as $R = R(\vec{k} = 0) + \vec{k}^2 R^{(2)} + \ldots$ and $\gamma = \gamma(\vec{k} = 0) + \vec{k}^2 \gamma^{(2)} + \ldots$. Some matrix algebra then leads to $F(\vec{k}) = F(\vec{k} = 0) + \vec{k}^2 F^{(2)} + \ldots$ from which[19]

$$b = 2\,\mathrm{tr}_p \Lambda_p(0) R_p^{(2)} \Lambda_p(0) + 2\,\mathrm{tr}_p \mathrm{tr}_{p'} [dG(p)/d\mu] \gamma_{pp'}^{(2)} dG(p')/d\mu,$$

(4)

where $dG(p)/d\mu = (\partial/\partial p_0 + \partial/\partial\mu) G(p)$ and $\Lambda_p(0) = dG^{-1}(p)/d\mu = 1 - d\Sigma(p)/d\mu$. This new relation for b (and hence for B_{xc}) is exact and is obviously very convenient for subsequent analysis as the complicated in-

tegral equations describing electron-hole corre-
lations have been solved exactly to order $\vec{k}^2$ and
expressed, so far as possible, in terms of the
one-electron propagator and its derivative.

The high-density limit of Eq. (4) is obtained by
expanding to the appropriate order in the dynam-
ically screened interaction and corresponds pre-
cisely to the $\vec{k}^2$ expansion of the graphs in Fig. 1
which were considered by Ma and Brueckner[11]
and by Sham.[12] Expressing b in the form $b = (2\pi)^{-3}$
$\times(em/\hbar^2 k_F)^2 Z$, the first-order exchange contribu-
tion[12] [Fig. 1(a)] is $Z_a = \frac{5}{9}$ while the total first-or-
der correlation contribution[11] [Figs. 1(b) and 1(c)]
is $Z_{bc} = 1.9756$. We have extended the calculation
of Ma and Brueckner to determine Z_b and Z_c sep-
arately[20]; the results are $Z_b = -0.0714$ and Z_c
$= 2.0470$. Obviously, screening the Hartree-Fock
graphs gives only a minor contribution to b, and
the correlation graphs of Fig. 1(c), which are
neglected in a simple Thomas-Fermi approxima-
tion,[14-16] are essential.

We now indicate an approximate evaluation of
Eq. (4) in the RPA at metallic densities. To il-
lustrate what is involved, consider the corre-
sponding calculation of $a^{-1} = -dn/d\mu = -(dn/d\mu_0)/$
$(1 + d\mu'/d\mu_0)$, where the RPA shift in chemical po-
tential, μ', can be obtained from the ground-
state energy. However, $F(k=0) = a^{-1}$ may also
be evaluated directly by expanding Eq. (3) in pow-
ers of the screened interaction. The first-order
RPA corrections (Fig. 1) are known[21] to contrib-
ute $F_0(0)(-d\mu'/d\mu_0)$, and higher-order graphs,
which are iterations of those in Fig. 1, may thus
be grouped to form a simple geometric series
which sums to $F(0) = F_0(0)/(1 + d\mu'/d\mu_0)$ as re-
quired by a Ward identity. Observe that this ex-
act result may also be simulated by the limiting
case of a short-range interaction, i.e., a Hub-
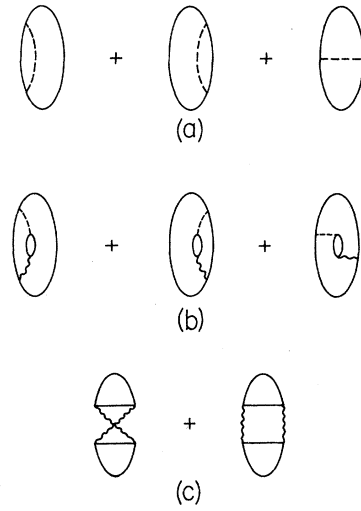bard[17] approximation to ladder graphs, with $v \to \bar{v}$

FIG. 1. First-order RPA contributions to the screen-
ing function due to (a) pure exchange, (b) screening of
exchange graphs, and (c) non-Hartree-Fock scattering
processes.

$= $const so that $\Sigma \to -\bar{v}n/2$, $\Lambda \to 1/(1-\eta)$, and $F(0)$
$\to F_0(0)/(1-\eta)$, where $\eta = -d\mu'/d\mu_0$. Now apply
the same procedure to Eq. (4). The first term on
the right-hand side, b_I, becomes $b \to b_0/(1-\eta)^2$
$= b_0 + 2\eta b_0(1 - \frac{1}{2}\eta)/(1-\eta)^2$. To adapt this form to
the electron gas, we must replace $2\eta b_0$ by the
correct first-order RPA $b_I^{(1)}$ as determined from
the graphs in Fig. 1 [the higher-order vertex en-
hancements are of the type entering $F(0)$ and are
not to be altered]. Higher-order vertex-function
corrections also enter the second term in Eq. (4),
b_{II}, since $dG(p)/d\mu = -G^2(p)\Lambda_p(0)$ and are again
consistently replaced by their average value, $1/$
$(1-\eta)$, so that $b_{II} \to b_{II}^{(1)}/(1-\eta)^2$. The required
values of $b_I^{(1)}$ and $b_{II}^{(1)}$ are obtained from the $\vec{k}^2$
expansion of the graphs in Fig. 1 and are $b_I^{(1)}$
$= b'(r_s) + b''(r_s) - (\mu'/\mu_0)b_0/2$ and $b_{II}^{(1)} = b'''(r_s)$,
where

$$b'(r_s) = -\frac{\hbar^2}{m}\frac{\partial}{\partial\mu_0}\operatorname{tr}_p\Sigma(p)\left(\frac{1}{2}\frac{d^2}{d\mu_0{}^2}G_0(p) - \frac{\epsilon_p}{9}\frac{d^3}{d\mu_0{}^3}G_0(p)\right),\tag{5}$$

$$b''(r_s) = (\hbar^2/m)\operatorname{tr}_p\Sigma(p)\left[\frac{1}{6}\frac{d^3G_0(p)}{d\mu_0{}^3}\right],\tag{6}$$

$$b'''(r_s) = \frac{1}{24}\operatorname{tr}_q[\partial F_0(q)/\partial\mu_0]^2\{[\nabla_q V(q)]^2 - V(q)\nabla_q{}^2 V(q)\},\tag{7}$$

and the RPA self-energy, $\Sigma(p)$, includes both ex-
change and correlation in contrast to Eq. (4.18)
of Ma and Brueckner. It must be emphasized that
Eqs. (5) to (7) must be evaluated without the sim-

plifying high-density approximations.[11] The cal-
culation is delicate and very lengthy; details will
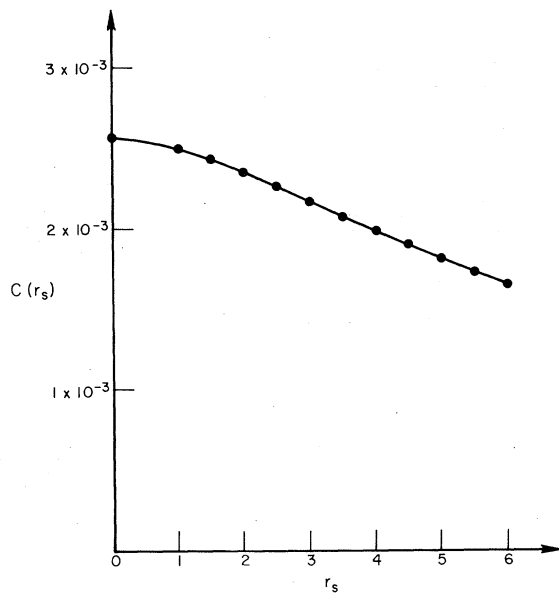be given elsewhere.[22] After appropriate transfor-

FIG. 2. Calculated r_s dependence, in the metallic density range, of $C(r_s)$ which determines the gradient coefficient $B_{xc} = C(r_s)e^2/n^{4/3}$.

mations, b', b'', and b''' were evaluated numerically for a range of values of r_s in the metallic density range. Data tabulated by Hedin and Lundqvist[23] were used for η and μ'. Using these results for $b = b_I + b_{II}$ in Eq. (2) than yields B_{xc} $= C(r_s)e^2/n^{4/3}$; $C(r_s)$ is plotted in Fig. 2. Note that the density dependence is substantial and that correlation effects, which have been consistently included within the RPA, are dominant in the entire density range.[24] These results permit the first fundamental investigation of the accuracy of the gradient expansion in metallic systems. Application of these results for B_{xc} to the problem of metallic surface energies has been very encouraging. For example, discrepancies of about 15% which exist between experiment and the local density approximation[25] for the surface energies of Mg and Li are completely removed by use of the present B_{xc} for gradient corrections.[26] Finally, note that in systems with discrete states, such as atoms, virtual transitions involve finite energy denominators and the associated correlation effects are smaller than in systems such as metals which have a continuum of low-energy excitations.[27] There is thus no contradiction in the fact that $B_{xc} < 0$ is found for atoms,[13] while $B_{xc} > 0$ is required in metallic surface problems[28] where correlation effects are dominant.

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[20]Ma and Brueckner were interested only in the total correlation effect and so did not calculate Z_b and Z_c separately. Their relative contribution is of interest, however, since in attempting to treat correlations by simply screening the exchange graphs in a Thomas-Fermi approximation Z_b is included (approximately) but Z_c is totally neglected.

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[24]It is extremely important that the higher-order vertex corrections in both a and b have been consistently treated as required by the Ward identities. To appreciate this point, recall that $a = -d\mu/dn = -d^2(n\epsilon)/dn^2$, where ϵ is the ground-state energy per electron. The general shape of ϵ as a function of density is well known and all calculations, including RPA, show that a vanishes for $r_s = r_{s0} > 5.5$ (see Refs. 21 and 23). The physical implications of this fact should not be naively misinterpreted since the electron gas and its positive background are constrained to have uniform density and are not mechanically closed systems in the thermodynamic sense, but we must still conclude that $F(0)$

$= a^{-1}$ and the vertex function are very large for $r_s \approx r_{s0}$. Our approximation has the important consequence that $B_{xc} = (a^2 b - a_0^2 b_0)/2$ remains finite and positive at $r_s = r_{s0}$, as expected on physical grounds.

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Observation of a Change in the Surface Electronic Structure of Pt(100) Induced by Reconstruction

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We investigated the clean surface of a Pt(100) single crystal in its stable (5 × 20) and metastable (1 × 1) configurations by ultraviolet photoelectron spectroscopy, Auger electron spectroscopy, and low-energy electron diffraction. The photoelectron spectrum of the (1 × 1) surface for $h\nu = 11.6$–40.8 eV is characterized by a narrow peak 0.25 eV below the Fermi level; it is suggested that this peak is due to a maximum in the surface density of states associated with an electronic surface resonance or surface state on the (1 × 1) surface.

Certain crystallographic orientations of Pt[1,2] and Au[3,4] are characterized by surface reconstruction, i.e., the surface structure is not equivalent to that resulting from a termination of the bulk lattice. The question of whether this reconstruction of Au(100) and Pt(100) surfaces into the (5 × 20) structure, as evidenced by low-energy electron diffraction (LEED), is related to the presence of surface impurities was highly controversial for a number of years.[5,6] More recently, considerable evidence was brought forward on the basis of Auger electron spectroscopy (AES) and metal-overlayer studies,[7,8] which indicates that the reconstructed surfaces are very clean and most likely representative of the equilibrium surface of these metals. If this is the case, one would expect the clean, unreconstructed Pt(100)-(1 × 1) surface, if it could be prepared, to exhibit a higher surface free energy and to be metastable. Furthermore, the difference in surface free energy and atom arrangment between the (1 × 1) and (5 × 20) surfaces should be accompanied by (and possibily due to) a difference in surface electronic structure.

In this Letter we report on the first successful preparation of the clean Pt(100)-(1 × 1) surface which we studied using AES, LEED, and ultraviolet photoelectron spectroscopy (UPS). We find that this surface is indeed metastable and has a surface electronic structure (as determined by UPS) which is considerably different from that of the (5 × 20) surface.

The experiments were performed on a well oriented, polished, Pt(100) single crystal (Marz grade, Materials Research Corporation) cleaned by *in situ* Ar-ion bombardment and high-temperature annealing up to 1100°C. The final surface was found to be free of impurities as judged from AES. The surface structure was characterized by a sharp (5 × 20) LEED pattern. This crystal was studied by UPS in the photon energy range 11.6–40.8 eV, with a dc resonance lamp using He, Ne, or Ar depending on which photon energy was desired. The angle of incidence of the photons was approximately 30° while the axis of the double-pass cylindrical-mirror analyzer (Physical Electronics Industries) made an angle of 15° with the sample normal. With this geometry, the measured electron energy distributions represent an average over polar angles of from approximately 27° to 52°. Other experimental details will be published elsewhere.[9]

As mentioned above, the equilibrium structure of a clean Pt(100) surface can be easily and reproducibly obtained by heating at elevated temperature, and it will always show a (5 × 20) LEED pattern.[2,10] On the other hand, the metastable (1 × 1) structure of a *clean* and well-annealed Pt(100) surface cannot be obtained by conventional techniques.

To obtain a clean (1 × 1) surface, one method we have used is a catalytic reaction between ad-