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Exchange and correlation energy of an inhomogeneous electron gas at metallic densities*

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A convenient expression is derived for the coefficient, $B_{xc}(n)$, which determines the first gradient corrections to the exchange and correlation energy of an inhomogeneous electron gas. The result is exact to all orders in e^2 and is expressed in terms of a single-particle propagator. The lowest-order contributions to B_{xc} are evaluated *without* the simplifying high-density approximation. The formal structure of the derived expression for B_{xc} is then used to develop an approximation method for including the contribution of all higher-order graphs within the random-phase approximation. Numerical results are given for B_{xc} in the metallic density range. Application to surface energy of metals show an improvement over any previous approximations for B_{xc}.

I. INTRODUCTION

In a series of three papers Hohenberg, Kohn, and Sham[1-3] have laid the foundations for a general theory of the inhomogeneous electron gas in the ground state. The theory is based on the fact that the ground-state wave function, and thus all ground-state properties (specifically the ground-state energy), are functionals of the density $n(\vec{r})$.

For the case in which the deviation from the uniform density n_0 [i.e., $\delta n(\vec{r}) \equiv n(\vec{r}) - n_0$] is slowly varying, but possibly large, Kohn and Sham[2] expand $E_{xc}(n)$ as a series in density gradients, i.e.,

$$E_{xc}(n(\vec{r})) = \int d\vec{r}\,[A_{xc}(n(\vec{r})) + B_{xc}(n(\vec{r}))\,|\nabla n(\vec{r})|^2] . \qquad (1)$$

For further discussion we separate the coefficients A_{xc} and B_{xc} into an exchange and a correlation contribution, given, respectively, by A_x and B_x, A_c and B_c.

Most calculations applying this expansion have been restricted to using only the first (local) term A_{xc}, since no reliable gradient term B_{xc} has been available at metallic densities. The need for B_{xc} at metallic densities is clearly reflected by the large number of papers in which various approximations have been introduced. Examples are found in surface physics problems,[4-7] electron-hole droplets,[8-10] cohesive energy of solids, etc. Some of these works use a form of B_{xc} evaluated from the electron-gas screening function $F(\vec{k})$. (See, e.g., Ma and Brueckner,[11] to be referred to as MB.) That is,

$$F(\vec{k}) = a^{-1} + b\vec{k}^2 + O(\vec{k}^4) \qquad (2)$$

in terms of which

$$B_{xc} = \tfrac{1}{2}(a^2 b - a_0^2 b_0) , \qquad (3)$$

where a_0 and b_0 refer to the small-$\vec{k}$ expansion of the Lindhard screening function and $a = -d\mu/dn$, where μ denotes the exact chemical potential. The difficulty lies in evaluating b in Eq. (2). It has been evaluated previously only in the high-density limit by Sham[12] for the exchange contribution (b_x), and by MB for the correlation part (b_c). Some other works use an empirically determined B_x, either adjusted to make the total energy, given by Eq. (1), equal to the full Hartree-Fock (HF) energy or a B_{xc} obtained by minimizing the energy expressed in the form of Eq. (1) (see Herman *et al.*[13]).

Since, as pointed out above, first-principles calculations of B_{xc}[11,12] were restricted to the high-density limit, the investigation of the validity of the gradient expansion [Eq. (1)] was restricted to systems with high density (atoms). In comparing the high density B_x with that obtained empirically, the latter was found to be approximately 3 times[12] too large. The difference was attributed to the neglect of higher gradient contributions.[14] Later calculations by Geldart and Rasolt,[15] Geldart, Rasolt, and Ambladh,[16] and Kleinman[17] showed that a first-principles B_x does not even exist. Thus the above comparison has no fundamental meaning. Furthermore, with the reasonable assumption that the full B_{xc} exists, it is clear that the separation of the exchange and correlation contributions in the gradient expansion is incorrect.[18]

Before we comment on B_c we wish to briefly mention the trends of the contribution of A_x and A_c in atomic calculations. While including A_x accounted for the full HF energy (see Tong and Sham[19]) to within 10%, the contribution of A_c grossly misrepresented the correlation part[19] (larger by a factor of 2). Returning to B_c, it was found by MB that its contribution in atoms was also too large, by approximately a factor of 5, and thus further worsened agreement with experiment. Finally, in applying Eq. (1) to surface energy calculations, it has been shown by Lang and Sham[20] that B_{xc} should be of opposite sign to that required in atoms (i.e., the empirical B_{xc} of Herman[13] *et al.*).

To understand the above trends, we refer to the work of Tong[21] in which he found that systems with discrete states are not appropriate for testing the validity of this expansion. More precisely, Tong has shown that it is especially the correlation part A_c (which involves energy denominators associated with virtual transitions, in contrast to the exchange part which does not) which is misrepresented in atoms and, as expected, is too large. Since A_{xc} is derived from the electron gas (a system with purely continuous states) its application to atoms is inappropriate. The same conclusion applies to B_{xc} with the additional constraint that the separation to B_x and B_c is meaningless (see above). From this discussion, it is clear that to properly ascertain the accuracy of the gradient expansion it is necessary to apply Eq. (1) to metallic systems. This requires that B_{xc} be evaluated at metallic densities, which is the purpose of this work.[22,23]

In Sec. II we derive a convenient expression for b in Eq. (2). The result is exact to all orders in e^2 and is expressed in terms of the single-particle propagators. The simplicity of this expression allows a fundamental analysis of B_{xc} at metallic densities.

In Sec. III we apply this expression to evaluating B_{xc} for an arbitrary static particle-particle interaction within the HF class of graphs.

In Sec. IV we evaluate the lowest-order graphs considered by MB without the simplifying high-density approximations.

In Sec. V, using the results of Secs. II and IV, we extend the calculation of B_{xc} to metallic densities. Some applications to the surface energy of metals and a conclusion follow.

II. GENERAL FORM FOR *b*

In this section we derive an expression for b [see Eq. (2)] which is exact to all orders in e^2. We start from the equation, in the usual matrix notation, for the reducible scattering function $\Gamma(\vec{k})$,[24] i.e.,

$$\Gamma(\vec{k}) = \gamma(\vec{k}) + \gamma(\vec{k}) R(\vec{k}) \Gamma(\vec{k}) \tag{4}$$

or

$$\Gamma(\vec{k}) = \Gamma(\vec{k}) + \Gamma(\vec{k}) R(\vec{k}) \gamma(\vec{k}) \ , \tag{5}$$

where $\gamma(\vec{k})$ is the irreducible scattering function and matrix elements of $R(\vec{k})$ are given by

$$R_{p,p'}(\vec{k}) = G(p + \tfrac{1}{2}\vec{k}) G(p - \tfrac{1}{2}\vec{k}) \delta_{p,p'} \ , \tag{6}$$

with G denoting the exact one-electron propagator, and $p = (\vec{p}, p_0)$. Now since b corresponds to the $\vec{k}^2$ term of $F(\vec{k})$ we next expand $\gamma(\vec{k})$ and $R(\vec{k})$ to that order, i.e.,

$$\gamma(\vec{k}) = \gamma(0) + \vec{k}^2 \gamma^{(2)} + O(\vec{k}^4) \tag{7}$$

and

$$R(\vec{k}) = R(0) + \vec{k}^2 R^{(2)} + O(\vec{k}^4) \ . \tag{8}$$

Some matrix algebra using Eqs. (4)–(7) yields

$$\begin{aligned} \Gamma(\vec{k}) - \Gamma(0) = {} & \Gamma(0) \vec{k}^2 R^{(2)} \Gamma(0) + [1 + \Gamma(0) R(0)] \\ & \times \vec{k}^2 \gamma^{(2)} [1 + R(0) \Gamma(0)] \ . \end{aligned} \tag{9}$$

Next we define a vertex function $\Lambda(\vec{k})$, given by

$$\Lambda(\vec{k}) = \lambda + \Gamma(\vec{k}) R(\vec{k}) \lambda \ , \tag{10}$$

where λ is a column vector with components $\lambda_p = 1$. In terms of $\Lambda(\vec{k})$, the screening function, is given by

$$F(\vec{k}) = 2 \tilde{\lambda} R(\vec{k}) \Lambda(\vec{k}) \ , \tag{11}$$

where $\tilde{\lambda}$ is the transpose of λ. Some matrix algebra, using Eqs. (9)–(11), yields

$$\begin{aligned} \vec{k}^2 b = {} & 2 \tilde{\Lambda}(0) \vec{k}^2 R^{(2)} \Lambda(0) + 2 \tilde{\lambda} R(0) [1 + \Gamma(0) R(0)] \\ & \times \vec{k}^2 \gamma^{(2)} [1 + R(0) \Gamma(0)] R(0) \lambda \ , \end{aligned} \tag{12}$$

where $\tilde{\Lambda}(0)$ is the transpose of $\Lambda(0)$. Noting that

$$-\frac{dG(p)}{d\mu} = [1 + R(0) \Gamma(0)] R(0) \lambda \ , \tag{13}$$

where

$$\frac{dG(p)}{d\mu} = \frac{\partial G(p)}{\partial p_0} + \frac{\partial G(p)}{\partial \mu} \ ,$$

we get the final expression for b

$$\begin{aligned} b = {} & 2 \mathrm{tr}_p \Lambda_p(0) R_p^2 \Lambda_p(0) \\ & + 2 \mathrm{tr}_p \mathrm{tr}_{p'} \frac{dG(p)}{d\mu} \gamma^{(2)}_{p,p'} \frac{dG(p')}{d\mu} \ , \end{aligned} \tag{14}$$

$$\mathrm{tr}_p(\cdots) \equiv \frac{d^4 p}{(2\pi)^4 i} (\cdots) \ ,$$

where the vertex function at $\vec{k} = 0$ is given by the Ward identity as

$$\Lambda_p(0) = \frac{dG^{-1}(p)}{d\mu} \ . \tag{14b}$$

This new relation for b (and hence for B_{xc}) is *exact* and is obviously very convenient, as the complicated equation describing the (two-body) electron-hole correlation has been solved exactly to order $\vec{k}^2$ and expressed, as far as possible, in terms of the one-electron propagators and its derivatives. The simplicity of the above expression will allow, in the following sections, a first fundamental study of B_{xc} at metallic densities. Without it, such analysis would be virtually im-possible.

We finally note that a more general expression for $F(k)$ appropriate to all powers of k^2 can be written down. Following almost identically the previous derivation, without the expansions in Eqs. (7) and (8), we get

$$F(k)-F(0)=+2\mathrm{tr}_p\Lambda_p(k)\,[R_p(k)-R_p(0)]\,\Lambda_p(0)+2\mathrm{tr}_p\mathrm{tr}_{p'}\Lambda_p(k)R_p(k)\times[\gamma(k)-\gamma(0)]R_{p'}(0)\Lambda_{p'}(0)\ , \tag{15}$$

where the appropriate limiting process for $k\rightarrow 0$ (i.e., $k_0\rightarrow 0, |\vec{k}|\rightarrow 0$) must be observed in $R_p(0)$ and $F(0)$. Equation (15) might be useful in studying the dynamic as well as the static properties of the screening function $F(k)$.

III. EXACT SOLUTION OF b FOR ARBITRARY STATIC PARTICLE-PARTICLE INTERACTION FOR THE HF CLASS OF GRAPHS

Before we apply Eq. (14) for the study of b in the presence of dynamically screened interaction (Secs. IV and V) we first wish to demonstrate the versatility of this expression by deriving an exact expression for b in the presence of an *arbitrary* spherically symmetrical static interparticle interaction for the HF set of graphs. These graphs are shown in Fig. 1, where each wavy interaction line now represents

$$\gamma_{p,p'}=-v(\vec{p}-\vec{p}\,') \tag{16}$$

and the electron lines denote self-consistent Hartree-Fock propagators.

That the set of graphs in Fig. 1 represent the HF screening function $F(\vec{k})$ is known; for completeness we demonstrate it briefly in Appendix A.

Returning to Eq. (14) we note first that the last term is now absent since the irreducible scattering function in Eq. (16) is independent of $\vec{k}$. Secondly, Λ_p is independent of p_0 and thus the integration over p_0 in Eq. (14) is easily evaluated. We get for b

$$b=2\int\frac{d^3p}{(2\pi)^3}\,\Lambda_{\vec{p}}R_{\vec{p}}^{(2)}\Lambda_{\vec{p}}(0)\ . \tag{17}$$

Now the HF self energy is given by

$$\Sigma(\vec{p})=-\int\frac{d^3p'}{(2\pi)^3}\,v(\vec{p}-\vec{p}\,')f(E(\vec{p}\,'))\ , \tag{18}$$

where $f(E(p))$ is the usual Fermi step function and the particle-dispersion law is

$$E(\vec{p})=\hbar^2\vec{p}^{\,2}/2m+\Sigma(\vec{p})\ . \tag{19}$$

The term $R_{\vec{p}}^{(2)}$ is the $\vec{k}^2$ expansion of Eq. (8) after integration of p_0. It is straightforward to show that $R_{\vec{p}}^{(2)}$ is thus simply the $\vec{k}^2$ term of $R_{\vec{p}}(\vec{k})$ given by

$$R_{\vec{p}}(\vec{k})=\int_{-\infty}^{+\infty}\frac{dp_0}{2\pi i}\,R_p(\vec{k})=\frac{f(E(\vec{p}+\frac{1}{2}\vec{k}))-f(E(\vec{p}-\frac{1}{2}\vec{k}))}{E(\vec{p}+\frac{1}{2}\vec{k})-E(\vec{p}-\frac{1}{2}\vec{k})}\ . \tag{20}$$

To get $R_{\vec{p}}^{(2)}$ from Eq. (20) we expand the Fermi step functions, $f(E(\vec{p}\pm\frac{1}{2}\vec{k}))$, in Eq. (20) to third order [because of the energy denominator in $E(\vec{p}\pm\frac{1}{2}\vec{k})-E(\vec{p})$] and then expand $E(\vec{p}\pm\frac{1}{2}\vec{k})$ to second order in $\vec{k}$ to obtain

$$\vec{k}^2R_{\vec{p}}^{(2)}=\tfrac{1}{8}f''(E(p))[(\vec{k}\cdot\nabla_{\vec{p}})^2E(p)]+\tfrac{1}{24}f''(E(p))[\vec{k}\cdot\nabla_{\vec{p}}E(p)]^2\ , \tag{21}$$

where we noted that $E(\vec{p})=E(p)$ is independent of angles. Inserting Eq. (21) in Eq. (17) and integrating over angles leads to

$$b=\frac{1}{24\pi^2}\int_0^\infty dp\,p^2[\Lambda(p)]^2\{[E''(p)+(2/p)E'(p)]\times f''(E(p))+\tfrac{1}{3}[E'(p)]^2f'''(E(p))\}\ . \tag{22}$$

Primes denote differentiation with respect to the indicated argument and $\Lambda(p)\equiv\Lambda_p(\vec{0})$ in order to condense the notation a bit. Since $f'(E(p))=-\delta(E(p)-\mu)$, where

$$\mu=\hbar^2p_F^2/2m+\Sigma(p_F)=\mu(p_F) \tag{23}$$

is the chemical potential, it is evidently easy to perform the integration in Eq. (22). After some algebra and converting derivatives with respect to $E(p)$ into derivatives with respect to p we obtain the form

$$b=\frac{1}{36\pi^2}\left[\Lambda^2\left(-\frac{2}{E'}-\frac{2pE''}{(E')^2}+\frac{p^2(E'')^2}{(E')^3}-\frac{p^2E'''}{(E')^2}\right)+\Lambda\Lambda'\left(-\frac{2p^2E''}{(E')^2}-\frac{2p}{E'}\right)+[(\Lambda')^2+\Lambda\Lambda'']\frac{p^2}{E'}\right], \tag{24}$$

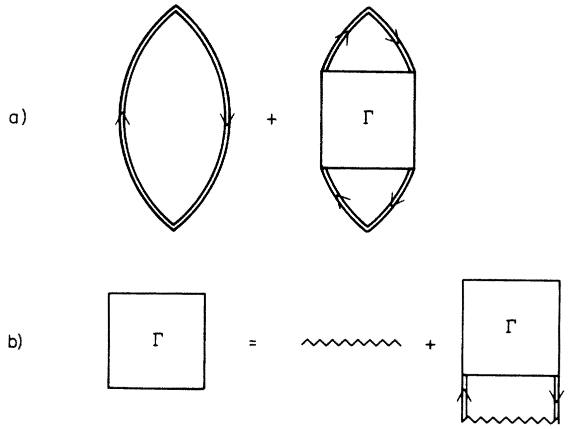

FIG. 1. Series of graphs for $F(k)$ in the self-consistent Hartee-Fock approximation. The wavy line represents the interparticle interaction.

where all functions and derivatives are evaluated at $p=k_F$. We note that Λ can also be expressed in terms of $E(\vec{p})$ via the Ward identity

$$\Lambda(\vec{p}) = 1 - \frac{\partial}{\partial\mu}\,\Sigma(\vec{p}) \tag{25}$$

from which

$$\Lambda(k_F) = E'(k_F)/\mu'(k_F)\ , \tag{26}$$

where $\mu'(k_F)$ is evaluated from Eq. (23). Eq. (24) is an exact closed form solution for b for an arbitrary $v(\vec{p}-\vec{p}\,')$. The form for b restricted to $v(\vec{p}-\vec{p}\,')$ of the Yukawa form, i.e.,

$$v(\vec{p}-\vec{p}\,') = 1/[(\vec{p}-\vec{p}\,')^2 + \lambda^2] \tag{27}$$

has been discussed in Refs. (15–17). From Eq. (24) the solution, however, is considerably more transparent and is derived in Appendix B. The final result is given in Eq. (B13).

We next use this result to discuss briefly two cases: the bare Coulomb interaction and the Thomas-Fermi (TF) screening, i.e.,

$$\lambda^2 = \lambda_{\mathrm{TF}}^2 = 4k_F/\pi a_0 \tag{28}$$

to attempt to discuss the case of a bare Coulomb interaction, consider the $\lambda\to 0$ limit. It is easy to see from Eq. (B11) that

$$4\pi e^2 b \xrightarrow[\lambda\to 0]{} + \frac{\ln\lambda^2}{18(\pi k_F a_0 - 1)^2} + \cdots\ . \tag{29}$$

Thus the *sum* of the Hartree-Fock series for b, which was calculated exactly in a nonperturbative way, is strictly divergent for bare Coulomb interactions (defined as the $\lambda\to 0$ limit of the corresponding Yukawa interaction).

It is apparent from Eq. (B11) that the perturbation expansion of powers of e^2 will also exhibit singularities. The usual perturbation expansion for b requires e^2, in appropriate units, to be small in order that the expansion of powers of e^2 be meaningful. The $\lambda\to 0$ limit is then to be taken term by term in the expansion so as to simulate the bare Coulomb interaction. Applying this procedure through order e^4 results in

$$4\pi e^2 b \xrightarrow[\lambda\to 0]{} + \frac{1}{18}\left(\frac{6}{\pi k_F a_0} + \frac{5}{(\pi k_F a_0)^2} - \frac{(\ln\lambda^2)^2}{2(\pi k_F a_0)^3} + \cdots\right)\ . \tag{30}$$

The divergent term arises from the e^4 contribution to b; higher-order terms also diverge in agreement with Eq. (29). The first term of Eq. (30) is just the Lindhard contribution, b_0, the second corresponds to the high-density exchange result of Sham,[12] i.e.,

$$4\pi e^2 b_{\mathrm{ex}} = \tfrac{5}{18}[1/(\pi k_F a_0)^2]\ . \tag{31}$$

As an attempt to include correlation contribution and also generate some feeling for the importance of the density dependence of the higher-order graphs in Fig. (1), previous works[15–17] screened the bare Coulomb potential with TF screening length. [See Eq. (28).] In the next sections, we will show that the above procedure totally misrepresents the correlation contributions and the density dependence of B_{xc}. For completeness we present below the results for the TF screening. Using Eqs. (B11)–(B13) with Eq. (28) we get

$$A^{\mathrm{TF}} = 5 + \left(1 - \frac{8}{\pi k_F a_0}\right)\ln(1+\pi k_F a_0) - \frac{4(\pi k_F a_0)^2 - \pi k_F a_0 - 3}{(\pi k_F a_0 + 1)^2} - 8\pi k_F a_0 \tag{32}$$

and

$$B^{\mathrm{TF}} = \frac{[2\pi k_F a_0 + 2 + 2/(\pi k_F a_0 + 1) - 4/\pi k_F a_0 \ln(1+\pi k_F a_0)]^2}{2\pi k_F a_0 - 2 + (1 + 2/\pi k_F a_0)\ln(1+\pi k_F a_0)}\ . \tag{33}$$

$\mu'(k_F)$, which is given by Eq. (B6), can be similarly expressed so that

$$4\pi e^2 b_{\mathrm{TF}} = \frac{-(A^{\mathrm{TF}} + B^{\mathrm{TF}})}{18[\pi k_F a_0 - 1 + (1/\pi k_F a_0)\ln(1+\pi k_F a_0)]^2}\ . \tag{34}$$

From Eq. (34), we can immediately obtain the corresponding B_{xc}^{TF} from Eq. (3) and the well known form for a^{-1}

$$a^{-1} = -k_F^2/\pi^2\mu'(k_F)\ . \tag{35}$$

Defining a convenient dimensional quantity

$$B_{xc}^{\mathrm{TF}} = C^{\mathrm{TF}}(r_s)e^2/n^{4/3}\ , \tag{36}$$

we plot $C^{\mathrm{TF}}(r_s)$ in Fig. 2 as a function of r_s [$r_s = (\alpha k_F a_0)^{-1}$ with $\alpha = (4/9\pi)^{1/3}$]. Note the strong density dependence of $C^{\mathrm{TF}}(r_s)$ which has dropped by a factor of 10 from the high-density limit given exactly by

$$C^{\mathrm{TF}}(r_s) \xrightarrow[k_F a_0\to\infty]{} -(7/432\pi)(3\pi^2)^{-1/3}\ . \tag{37}$$

This suggests that the density dependence of $C(r_s)$ may be substantial and the remainder of this paper is devoted to obtaining a reliable estimate, with a consistent treatment of exchange and correlation, of $C(r_s)$ at metallic densities.

IV. FIRST-ORDER RANDOM-PHASE-APPROXIMATION EXCHANGE AND CORRELATION CONTRIBUTION TO b

In this section we evaluate the first-order correlation contribution to b *without the simplifying* high-density approximation. The lowest-order exchange contribution to b (b_{ex}) shown in Fig. 3(a) has been evaluated in Sec. III Eq. (31). The correlation contribution b_c is due to dynamically

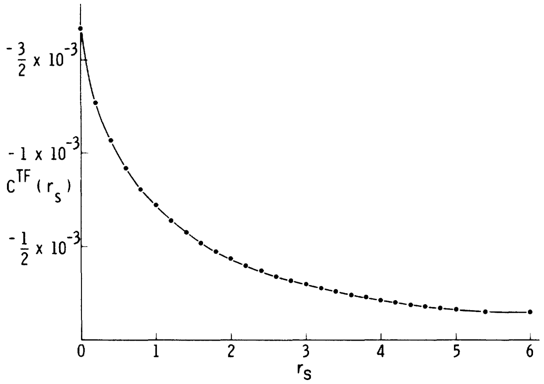

FIG. 2. Calculated r_s dependence of $C^{TF}(r_s)$ which is related to the B_{xc}, in the Thomas-Fermi approximation, by $B_{xc}=C^{TF}(r_s)e^2/n^{4/3}$.

screening the HF graphs, Fig. 3(b), and to the non-HF scattering process in Fig. 3(c). In the following calculation, for the sake of brevity, we follow the notation in MB who have carried out this calculation only in the high-density limit. The contributions of Figs. 3(b) and 3(c) are easily obtained by expanding Eq. (14) to the appropriate order in the dynamically screened interaction. The contributions of the first two graphs in Fig. 3(b) are obtained by setting the vertex function $\Lambda_p(0)$ equal to 1 and expanding Eq. (6) to first order in the self-energy. An expansion to order $\vec{k}^2$ and standard manipulation with the free-electron Green's function

$$G_0(p)=[p_0-\epsilon_{\vec{p}}+\mu_0+i\delta\,\mathrm{sgn}(\epsilon_{\vec{p}}-\mu_0)]^{-1}\,, \qquad (38)$$

where $\epsilon_{\vec{p}}=\hbar^2\vec{p}^2/2m$ and $\mu_0=\hbar^2k_F^2/2m$ (see MB) yields

$$b^{(1)}\vec{k}^2=\hbar^2\frac{\vec{k}^2}{m}\,\mathrm{tr}_p\left[\Sigma(p)\left(-\frac{1}{3}\frac{\partial^3}{\partial\mu_0^3}G_0(p)+\frac{1}{9}\epsilon_{\vec{p}}\frac{\partial^4}{\partial\mu_0^4}G_0(p)\right)\right]-\frac{\vec{k}^2\Sigma(k_F,0)}{24\pi^2\hbar v_0\mu_0}\,, \qquad (39)$$

where

$$\Sigma(p)=-\mathrm{tr}_{p'}[V^{-}(p')G_0(p+p')]\,, \qquad (40)$$

with

$$V^{-}(p')=\frac{4\pi e^2}{\vec{p}'^2}\left(\frac{1}{\epsilon(p')}-1\right) \qquad (41)$$

and $\epsilon(p')$ is the dielectric constant in the random-phase approximation (RPA). [In Eq. (39) $v_0=\hbar k_F/m$.]

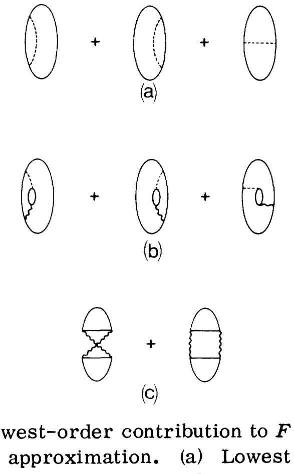

FIG. 3. Lowest-order contribution to $F(k)$ in the random-phase approximation. (a) Lowest order Hartree-Fock graphs; the dotted line represents the bare Coulomb interaction. (b) Lowest-order dynamic connections to the Hartree-Fock type of graphs; the wavy line represents the dynamically screened Coulomb interaction. (c) Lowest-order non-Hartree-Fock class of graphs.

The contribution of the third graph in Fig. 3(b) is obtained by approximating the vertex function in Eq. (14) with that of Fig. 4(a) and expanding Eq. (6) to power $\vec{k}^2$ and zero order in the interaction. We then get

$$b^{(2)}\vec{k}^2=\frac{\hbar^2\vec{k}^2}{m}\,\mathrm{tr}_p\left[\Lambda_p^{(2)}\left(\frac{1}{2}\frac{\partial^2}{\partial\mu_0^2}G_0(p)-\frac{1}{9}\epsilon_{\vec{p}}\frac{\partial^3}{\partial\mu_0^3}G_0(p)\right)\right]. \qquad (42)$$

Similarly the contribution from Fig. 3(c) is obtained by approximating the vertex function with that of Fig. 4(b). We get

$$b_2^{(3)}\vec{k}^2=\frac{\hbar^2\vec{k}^2}{m}\,\mathrm{tr}_p\left[\Lambda_p^{(3)}\left(\frac{1}{2}\frac{\partial^2}{\partial\mu_0^2}G_0(p)-\frac{1}{9}\epsilon_{\vec{p}}\frac{\partial^3}{\partial\mu_0^3}G_0(p)\right)\right]. \qquad (43)$$

There is an additional contribution to b from the $\vec{k}$ dependence of the irreducible scattering function (Fig. 4(c)—last two terms). This contribution simply corresponds to the last term of Eq. (14) with G replaced by G_0. After some algebra we get

$$b_1^{(3)}\vec{k}^2=b'''\vec{k}^2=\frac{-\hbar^2}{24}\vec{k}^2\,\mathrm{tr}_p\left\{\left(\frac{\partial}{\partial\mu_0}F^0(p)\right)^2\times\left[V(p)\nabla_{\vec{p}}^2V(p)-\left(\frac{d}{d\vec{p}}V(p)\right)^2\right]\right\}, \qquad (44)$$

where

$$V(p)=4\pi e^2/\vec{p}^2\epsilon(p) \qquad (45)$$

and $F^0(p)$ is the dynamic RPA screening function related to $\epsilon(p)$ by $\epsilon(p)=1-(4\pi e^2/\vec{p}^2)F^0(p)$. (See Appendix C.)

Adding all the contributions, b_c is given by

$$b_c=b^{(1)}+b^{(2)}+b_1^{(3)}+b_2^{(3)}\,. \qquad (46)$$

Following MB, it is convenient to rewrite b_c as

$$b_c=b'+b''+b'''-\Sigma(k_F,0)/24\pi^2\hbar v_0\mu_0\,, \qquad (47)$$

where a bit of algebra using the identity

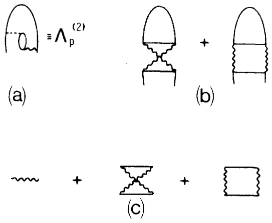

FIG. 4. (a) Lowest-order dynamic contribution to the Hartree-Fock vertex function. (b) Lowest-order non-Hartree-Fock vertex function. (c) The irreducible scattering function in the random-phase approximation.

$$\Lambda_p^{(2)} + \Lambda_p^{(3)} = -\frac{\partial \Sigma(p)}{\partial \mu_0} \tag{48}$$

yields

$$b' = -\frac{\hbar^2}{m} \frac{\partial}{\partial \mu_0} \operatorname{tr}_p \left[\Sigma(p) \left(\frac{1}{2} \frac{\partial^2}{\partial \mu_0^2} G_0(p) - \frac{1}{9} \epsilon_{\vec{p}} \frac{\partial^3}{\partial \mu_0^3} G_0(p) \right) \right] \tag{49}$$

and

$$b'' = \frac{\hbar^2}{m} \frac{1}{6} \operatorname{tr}_p \left(\Sigma(p) \frac{\partial^3}{\partial \mu_0^3} G_0(p) \right) . \tag{50}$$

We wish to point out that for the subsequent discussion the term $b_2^{(3)}$ will need to be evaluated separately, otherwise we could have gone directly to b', b'', and b'''. It must be emphasized, however, that separating the contributions of different graphs to $b' = b^{(1)} + b_2^{(3)}$ is meaningful *only* in the high-density limit. For finite densities, this separation is inappropriate (see Sec. V and Appendix D).

Before proceeding to calculate b_c without the simplifying high-density expansion, we wish to analyze, in the high-density limit, the following points. We mentioned in Sec. III that as an attempt to treat correlations, previous works[15-17] simply screened the HF class of graphs, Figs. 3(a) and 3(b), in the TF approximation. It is precisely the contributions of $b_1^{(3)}$ and $b_2^{(3)}$ which are therefore neglected. The relative contributions of $b^{(1)} + b^{(2)} \equiv b^{(1,2)}$ and of $b_2^{(3)} + b_1^{(3)} \equiv b^{(3)}$ are thus of considerable interest, since it would reflect how well the TF screening (Sec. III) incorporates the correlation contributions. Now MB were interested in the total b_c so did not need to calculate $b^{(1,2)}$ and $b^{(3)}$ separately. To evaluate $b_2^{(3)}$ we return to Eq. (43). After some rearrangement of terms we get

$$\begin{aligned} b_2^{(3)} = -\frac{\hbar^2}{m} \operatorname{tr}_{p'} \Bigg\{ & \frac{4\pi e^2}{|\vec{p}\,'|^2} \frac{\partial}{\partial \mu_0} \frac{1}{\epsilon(p')} \operatorname{tr}_p \Bigg[G_0(p+p') \\ & \times \left(-\frac{1}{2} \frac{\partial^2}{\partial \mu_0^2} G_0(p) + \frac{1}{9} \epsilon_{\vec{p}} \frac{\partial^3}{\partial \mu_0^3} G_0(p) \right) \Bigg] \Bigg\} . \end{aligned} \tag{51}$$

A considerable amount of algebra (see Appendix D) using procedures similar to those of MB yields for $b_2^{(3)}$ in the high-density limit

$$b_2^{(3)} = (2\pi)^{-3} (e/\hbar v_0)^2 Z_2^{(3)} , \tag{52}$$

with

$$Z_2^{(3)} = \frac{2}{9\pi} \int_0^\infty dy \frac{y^2(13+9y^2)}{R(y)(y^2+1)^4} = 1.4556 ,$$

where

$$R(y) = 1 - y \tan^{-1}(1/y) . \tag{53}$$

MB calculated $b_1^{(3)}$ and found the corresponding $Z_1^{(3)} = 0.5914$. Consequently, $Z^{(3)} = 2.0470$ whereas, from the total b_c (see MB) $Z^{(1,2)} = -0.0714$. It is obvious then that screening the HF graphs gives only a very minor correlation to b and that the non-HF graphs are essential. Thus, as pointed out in Sec. III, the TF approximation totally misrepresents the density dependence of B_{xc} (Fig. 2). A similar, but less extreme, situation exists for the relative contributions[25] of the graphs of Fig. 3 to a^{-1}.

As a final comment on the high-density limit, it should be noted that the qualitative argument in Sec. II of MB to show that correlation contributions to B_{xc} are of order e^2 is not correct, since their expansion of $n(\vec{x}+\frac{1}{2}\vec{r})$ to only first order in $\nabla n(\vec{x})$ is not sufficient to obtain all terms of order $|\nabla n(\vec{x})|^2$ in an expansion of the form of Eq. (1). If a consistent expansion is made for the *total* B_{xc}, it can be shown that $B_{xc} = 0$ is the resulting estimate. Thus, such agreements do suggest correctly that exchange and correlation contributions are of opposite sign and of the same order in e^2, but are otherwise inadequate.

To evaluate b', b'', and b''' is a considerable task. In Appendix C we give, as an example, some of the details involved in calculating b'. Below we simply quote the final results.

We first define the following functions:

$$g(q,y) = \ln\left(\frac{y^2+(q+1)^2}{y^2+(q-1)^2} \right) , \tag{54}$$

$$Q(q,y) = 2 + \frac{y^2+1-q^2}{2q} g(q,y) - 2y \left[\tan^{-1}\left(\frac{1+q}{y} \right) + \tan^{-1}\left(\frac{1-q}{y} \right) \right] , \tag{55}$$

$$\tilde{\epsilon}(q,y) = q^2 + (\alpha r_s/4\pi)\, Q(q,y) , \tag{56}$$

$$I_2'(q,y)=\frac{q^2y^2-\frac{1}{4}(y^2+1-q^2)(3+2q^2)}{(y^2+1-q^2)^2+4y^2q^2}+\frac{(\frac{3}{4}-q^2)[(y^2+1-q^2)^2-4y^2q^2]+4y^2(y^2+1-q^2)(\frac{3}{4}+q^2)}{[(y^2+1-q^2)^2-4y^2q^2]^2+16y^2q^2(y^2+1-q^2)^2}\ , \tag{57}$$

and

$$F(q,y)=\frac{(\frac{1}{6}-\frac{5}{18}q^2)(y^2+1-q^2)+\frac{1}{9}y^2(2+5q^2)}{(y^2+1-q^2)^2+4y^2q^2}+\frac{\frac{1}{9}y^2[4y^2q^2-(y^2+1-q^2)^2+2(y^2+1-q^2)(y^2-q^2)]}{[(y^2+1-q^2)^2-4y^2q^2]^2+16y^2q^2(y^2+1-q^2)^2}$$
$$-\tfrac{1}{24}(1/q)g(q,y)+\tfrac{1}{9}I_2'(q,y)\ , \tag{58}$$

then

$$b'=\frac{e^2}{18\pi^4(\hbar v_0)^2}\int_0^\infty dy\frac{y^2(9y^2+13)}{(y^2+1)^3}-\frac{e^4}{2\pi^5}\frac{1}{(\hbar v_0)^3}\left[\int_0^\infty dq\,q\int_0^\infty dy\frac{Q(q,y)F(q,y)}{[\tilde{\epsilon}(q,y)]^2}+\frac{\pi}{72}\left(1+\frac{\alpha r_s}{2\pi}\right)^{-2}\right]\ , \tag{59}$$

$$b''=\frac{1}{6}\frac{e^2\alpha r_s}{\pi^5(\hbar v_0)^2}\left[\int_0^\infty\frac{dq}{q}\int_0^\infty dy\frac{Q(q,y)}{\tilde{\epsilon}(q,y)}I_2'(q,y)+\frac{\pi}{8}\left(1+\frac{\alpha r_s}{2\pi}\right)^{-1}\right]\ , \tag{60}$$

and

$$b'''=\frac{e^4}{96\pi^5(\hbar v_0)^3}\int_0^\infty\frac{dq}{q}\int_0^\infty dy\frac{[g(q,y)]^2}{[\tilde{\epsilon}(q,y)]^2}\left(-1+\frac{\alpha r_s}{2\pi\tilde{\epsilon}(q,y)}\left\{4-\tfrac{3}{2}Q(q,y)+\frac{(q^2+y^2)(3y^2-q^2+1)}{(y^2-q^2+1)^2+4y^2q^2}\right.\right.$$
$$\left.+\left[q-\frac{7}{4}\left(\frac{q^2+y^2}{q}\right)\right]g(q,y)\right\}+\frac{(\alpha r_s)^2}{8\pi^2[\tilde{\epsilon}(q,y)]^2}\left\{4+Q(q,y)\left[\tfrac{9}{4}Q(q,y)-6+\frac{3}{2}\left(\frac{q^2+y^2}{q}\right)g(q,y)\right]\right.$$
$$\left.\left.+g(q,y)\left(\frac{(q^2+y^2)^2}{4q^2}g(q,y)-2\frac{(q^2+y^2)}{q}\right)\right\}\right)\ . \tag{61}$$

We note that Eqs. (59)–(61) reduce to the proper high-density limit (see MB).

In Sec. V we use these b', b'', and b''' in extending the calculation of b (or equivalently B_{xc}) to metallic densities.

V. EVALUATION OF B_{xc} AT METALLIC DENSITIES

In this section we wish to extend the calculation of $b_{ex}+b_c$ of Secs. III and IV to the metallic range. Before proposing an approximate scheme for doing this we briefly comment on $F(0)$ (or a^{-1}). We first recall that a^{-1} is proportional to the compressibility which is directly related to the second density derivative of the energy. Thus one can obtain the RPA a^{-1} from the available calculations of the electron-gas energy in the RPA. A second approach would entail direct calculation of the $\vec{k}\to 0$ limit of $F(\vec{k})$. In other words, calculate the sum of the set of graphs in Fig. 1 with the interaction now replaced by the irreducible scattering function of Fig. 4(c) with $\vec{k}=0$ and the propagators dressed with the RPA self-energy. An essential point to note is that a^{-1} as calculated from the ground-state energy is a very strong function of the density and, in fact, becomes singular at $r_s=r_{s0}\gtrsim 5$. Thus for the direct calculation of $F(0)$ to agree, the correct vertex-function enhancement (the infinite set of higher-order contributions of Fig. 1) is crucial. To stop at some lowest order would totally misrepresent a^{-1} in the metallic range.

In this work we are attempting to generate $a\,b$, or equivalently, B_{xc} by procedures closely analogous to those which yield reliable estimates of A_{xc} in the RPA. It is immediately apparent from the structure of Eq. (14) that b depends *quadratically* on the vertex function (which is the origin of the density-dependent-enhancement effect in a^{-1}). Hence, b is expected to be also a strong function of the density. To include these higher-order effects in b, we will be closely guided by Eq. (14). We demand that our approximations satisfy the following constraints.

(i) The lowest-order graphs, the Lindhard and first-order RPA contributions must be given exactly.

(ii) The higher-order contributions to b must be well defined functions of r_s (i.e., the relevant integrals contain no divergences, when properly grouped, see below) to all orders. However, the *sum* of these higher-order contributions can be singular at $r_s=r_{s0}$.

(iii) B_{xc} must be finite even though b is expected to diverge at $r_s=r_{s0}$ (i.e., the term a^2b in Eq. (3) is finite). In other words, the first gradient correction to the energy is assumed, on physical grounds, to be finite.

We next focus on the first term in the right-hand side of Eq. (14) which we denote by $b_{\rm I}$, i.e.,

$$b_{\rm I}=+2\,\mathrm{tr}_p\Lambda_p(0)R_p^{(2)}\Lambda_p(0)\ . \tag{62}$$

We write

$$\Lambda_p(0)=1+\tilde{\Lambda}_p(0) \tag{63}$$

(i.e., $\tilde{\Lambda}_p(0)$ contains all of the interaction effects).

Equation (62) can then be written

$$b_{\rm I} = 2\,{\rm tr}_p\{1 + 2\tilde{\Lambda}_p(0) + [\tilde{\Lambda}_p(0)]^2\}R_p^{(2)} . \qquad (64)$$

We next make the following two approximations: (i) We treat the coupling of $R_p^{(2)}$ to the first-order part of $\Lambda_p(0)$ exactly while the additional higher-order contributions from $\tilde{\Lambda}_p(0)$ are kept in an average way in the spirit of the Hubbard[26] approximation. (ii) For the moment we replace the exact $R_p^{(2)}$ with that evaluated from the free propagators (i.e., $G \to G_0$).

Before we apply the above approximations to Eq. (64) we briefly elaborate on their relation to the Hubbard[26] approximation. In its simplest form, this approximation replaces $\gamma_{p,p'}$ by an effective constant interaction. Let us denote this effective interaction by $-2\sigma(r_s)$, then the *full* $F(\vec{k})$ is given by

$$F(\vec{k}) = \frac{F_0(\vec{k})}{1 + \sigma(r_s)F_0(\vec{k})} \xrightarrow[\vec{k}\to 0]{} F(0) = \frac{a_0^{-1}}{1 + \sigma(r_s)a_0^{-1}} . \qquad (65)$$

Clearly, $\sigma(r_s)$ may be determined by requiring that $F(0)$ in Eq. (65) correctly reproduce a^{-1} for the range of r_s of interest (for convenience, define $\eta = -\sigma(r_s)a_0^{-1}$). Note that this result is also obtained directly from Eq. (11) for $\vec{k} \to 0$ by replacing the propagators by G_0 and the vertex function by $(1-\eta)^{-1}$ as in (i) and (ii) above.

Now returning to Eq. (64) and using the above discussion, we keep the first-order RPA contribution exactly and approximate the higher-order contributions to $\tilde{\Lambda}_p(0)$ in an average way by a factor of $(1-\eta)^{-1}$. The three terms in the right-hand side of Eq. (64) then become

$$b_{\rm I} = b_0 + b_{\rm I}^{(1)}\frac{1}{1-\eta} + b_{\rm I}^{(1)}\frac{\frac{1}{2}\eta}{(1-\eta)^2} , \qquad (66)$$

where

$$b_{\rm I}^{(1)} = b_{\rm ex} + b' + b'' - \Sigma(k_F, 0)/24\pi^2\hbar v_0\mu_0 \qquad (67)$$

and b' and b'' are given in Sec. IV. Note that in $b_{\rm I}^{(1)}$ we have also included the first-order contribution from the self-energies in the full propogators in $R_p^{(2)}$. The way this happens is clear from the perturbation expansion of Sec. IV. The approximation of Eq. (62) assumes that the self-energy and vertex corrections occur in essentially the same way in higher-order graphs. This procedure is motivated in part by the fact that the separation of $b^{(1)}$ [i.e., first two graphs of Fig. 3(b)] into contributions from self-energy and vertex contributions individually has no meaning at metallic density since the integrand of $b^{(1)}$ diverges (see Appendix D), even though a properly screened Coulomb interaction enters and careful grouping must be maintained in the full sum [see constraint (ii)], to obtain finite results. Similar cancellation of divergences occurs also in calculating a^{-1} although they are of different origin.[25]

We next turn to the second term of Eq. (14) which we denote by $b_{\rm II}$. To maintain a consistent analysis, we again replace the full propagator by $G \to G_0$ and include higher-order effects by treating the vertex function in an average way by

$$\frac{dG}{d\mu} = -R(0)\Lambda(0) \approx \frac{1}{1-\eta}\frac{\partial G_0}{\partial \mu_0} , \qquad (68)$$

then

$$b_{\rm II} = b'''/(1-\eta)^2 , \qquad (69)$$

or finally

$$b = b_0 + b_{\rm I}^{(1)}(1 - \tfrac{1}{2}\eta)/(1-\eta)^2 + b'''/(1-\eta)^2 , \qquad (70)$$

where b''' is given in Sec. IV.

It is interesting to compare Eq. (70) with Eq. (65) in the limiting case of a short-range interaction. From Eq. (65), the appropriate b is seen to be $b = b_0/(1-\eta)^2$ while the first-order correction $b_{\rm I}^{(1)} = 2\eta b_0$. Returning to Eq. (70), and realizing that $b''' = 0$, we substitute this $b_{\rm I}^{(1)}$ and retrieve the correct b.

To get B_{xc} we simply substitute Eq. (70) in Eq. (3). We note that the singularity in b, when $\eta = 1$, is precisely cancelled by a in Eq. (3) [a is given in Eq. (65) and thus leaves B_{xc} finite for all r_s as required].

After appropriate transformations, the integrals for b', b'', and b''' were evaluated numerically for a range of values of r_s in the metallic density range. The required values of $\Sigma(k_F, 0)$ and η were taken from the review article of Hedin and Lundquist.[27] It is convenient to express B_{xc} in the form $B_{xc} = C(r_s)e^2/n^{4/3}$ and we have plotted our results for $C(r_s)$ as a function of r_s in Fig. 5. Note that the density dependence is substantial (there is a 35% reduction in going from the high-density limit to $r_s = 6$). Also $C^{\rm TF}(r_s)$ (Fig. 2) is totally different from $C(r_s)$, and even of opposite sign throughout all r_s, reemphasizing that the Thomas-Fermi approximation is totally inadequate. Application of $C(r_s)$ to surface energy problems yields better agreement with experiment[28] than obtained in setting $B_{xc} = 0$ or using any other available approximations. For example, discrepancies of about 15% which exist between experiment and theory for the surface energies of Mg and Li (Ref. 29) are completely removed by use of the present B_{xc} for gradient corrections.[30]

In conclusion the present B_{xc} is consistently calculated within the RPA. Our experience with its RPA analog A_{xc} strongly suggests that such calculations are accurate to about 10%. Although some approximations had to be introduced in extending b to metallic range, we view this as a first fundamental analysis of B_{xc} for finite r_s. We also feel that by using Eq. (14), further improvements of

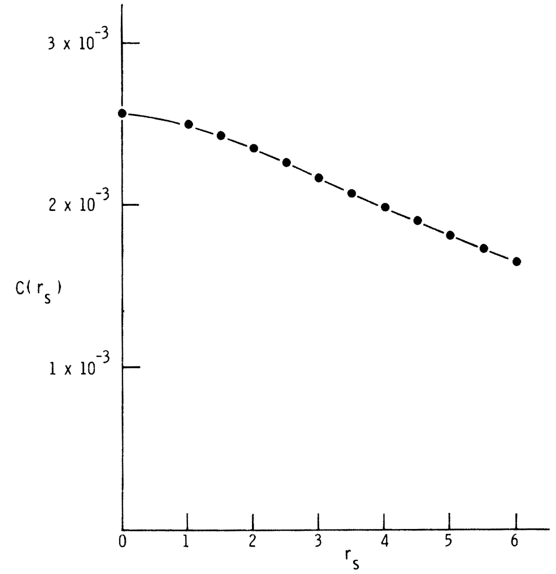

FIG. 5. Calculated r_s dependence of $C(r_s)$ which is related to the gradient coefficient B_{xc} by $B_{xc}=C(r_s)e^2/n^{4/3}$.

B_{xc} are possible. Just as considerable analysis of A_{xc} followed the original work by Gell-Mann and Brueckner[31] we hope that this work will initiate similar refinements in the analysis of B_{xc}.

APPENDIX A

The self-consistent Hartree-Fock equations are

$$\left(-\frac{\hbar^2}{2m}\nabla^2+V(\vec{r})+\int v(\vec{r}-\vec{r}\,')\rho(\vec{r}\,')\,d^3r'\right)\psi_{\vec{k}}(\vec{r})-\int v(\vec{r}-\vec{r}\,')\rho(\vec{r},\vec{r}\,')\psi_{\vec{k}}(\vec{r}\,')\,d^3r'=E_{\vec{k}}\psi_{\vec{k}}(\vec{r})\ , \tag{A1}$$

where $\rho(\vec{r})$ and $\rho(\vec{r},\vec{r}\,')$ are given self-consistently by

$$\rho(\vec{r})=2\sum_{\vec{k}=0}^{\vec{k}_F}\psi_{\vec{k}}^*(\vec{r})\,\psi_{\vec{k}}(\vec{r})\ ,$$

$$\rho(\vec{r},\vec{r}\,')=\sum_{\vec{k}=0}^{\vec{k}_F}\psi_{\vec{k}}(\vec{r})\,\psi_{\vec{k}}^*(\vec{r}\,')\ .$$

$V(\vec{r})$ is an arbitrary external potential, $v(\vec{r})$ is an arbitrary form of interparticle interaction, and $E_{\vec{k}}$ is defined in Eq. (19). We next expand $\psi_{\vec{k}}(\vec{r})$ in powers of $V(\vec{r})$, i.e.,

$$\psi_{\vec{k}}(\vec{r})=\psi_{\vec{k}}^{(0)}(\vec{r})+\psi_{\vec{k}}^{(1)}(\vec{r})\cdots\ . \tag{A2}$$

Keeping linear terms of $V(\vec{r})$ in (A1) and taking the Fourier transform we get

$$(E_{\vec{k}+\vec{q}}-E_{\vec{k}})\,\phi_{\vec{k}}(\vec{k}+\vec{q})-\sum_{\vec{k}'=0}^{\vec{k}_F}v(\vec{k}+\vec{q}-\vec{k}')\,\phi_{\vec{k}'}(\vec{k}'-\vec{q})$$

$$-\sum_{\vec{k}'=0}^{\vec{k}_F}v(\vec{k}-\vec{k}')\phi_{\vec{k}'}(\vec{k}'+\vec{q})+v(\vec{q})\delta\rho(\vec{q})+V(\vec{q})=0\ , \tag{A3}$$

where

$$\phi_{\vec{k}}(\vec{p})=\int\psi_{\vec{k}}^{(1)}(\vec{r})\,e^{i\vec{p}\cdot\vec{r}}\,d^3r\ .$$

In deriving (A3) we used the property $\phi_{\vec{k}}(\vec{p})=\phi_{-\vec{k}}(-\vec{p})$ on specializing to spherically symmetrical potentials. In (A3) $\delta\rho(\vec{q})$ is given by

$$\delta\rho(q)=2\sum_{\vec{k}=0}^{\vec{k}_F}[\phi_{\vec{k}}(\vec{k}+\vec{q})+\phi_{\vec{k}}(\vec{k}-\vec{q})]\ . \tag{A4}$$

We now define

$$\phi_{\vec{k}}(\vec{k}+\vec{q})=-\frac{\tilde{\Lambda}_{\vec{k}}(\vec{q})V(q)}{\epsilon(q)(E_{\vec{k}+\vec{q}}-E_{\vec{k}})}\ , \tag{A5}$$

where

$$\begin{gathered}\epsilon(q)=1+v(q)\pi(q)\ ,\\ \pi(q)=-2\int\tilde{R}_{\vec{k}'}(\vec{q})\tilde{\Lambda}_{\vec{k}'}(\vec{q})\,\frac{d^3k'}{(2\pi)^3}\ ,\end{gathered} \tag{A6}$$

and

$$\tilde{R}_{\vec{k}'}(\vec{q})=\frac{f(E(\vec{k}'+\vec{q}))-f(E(\vec{k}'))}{E(\vec{k}'+\vec{q})-E(\vec{k}')}\ .$$

Substituting (A5) in (A4) gives

$$\delta\rho(q)=-\pi(q)V(q)/\epsilon(q) \tag{A7}$$

Substituting (A5) and (A7) in (A3) gives

$$\tilde{\Lambda}_{\vec{k}}(\vec{q})=1-\int v(\vec{k}-\vec{k}')\tilde{R}_{\vec{k}'}(\vec{q})\tilde{\Lambda}_{\vec{k}'}(\vec{q})\,\frac{d^3k'}{(2\pi)^3} \tag{A8}$$

which completes the proof. [In deriving (A6) and (A7) we used the relation $\tilde{\Lambda}_{\vec{k}',-\vec{q}}(\vec{q})=\tilde{\Lambda}_{\vec{k}'}(-\vec{q})$ which is seen to be consistent with (A8).] Note that Eqs. (A6) and (A8) can be transformed into the more symmetrical form by the change of variables: $\vec{k}\to\vec{k}-\frac{1}{2}\vec{q}$ and $\vec{k}'\to\vec{k}'-\frac{1}{2}\vec{q}$.

APPENDIX B

In this appendix we evaluate Eq. (24) for interparticle interaction of Eq. (27). We require the self-energy which is found from Eq. (18) to be

$$\Sigma(p)=-\frac{e^2}{\pi}\left\{k_F+\frac{k_F^2+\lambda^2-p^2}{4p}\ln\left(\frac{(p+k_F)^2+\lambda^2}{(p-k_F)^2+\lambda^2}\right)-\lambda\left[\tan^{-1}\left(\frac{p+k_F}{\lambda}\right)-\tan^{-1}\left(\frac{p-k_F}{\lambda}\right)\right]\right\}\ . \tag{B1}$$

Setting $p=k_F$, the shift in chemical potential, according to Eq. (23), is given by

$$\delta\mu(k_F)=\Sigma(k_F)=-\frac{e^2}{\pi}\left[k_F+\frac{\lambda^2}{4k_F}\ln\left(\frac{4k_F^2+\lambda^2}{\lambda^2}\right)-\lambda\tan^{-1}\left(\frac{2k_F}{\lambda}\right)\right]\ . \tag{B2}$$

The required derivatives of Eq. (B1) are given by

$$\Sigma'(k_F)=\frac{e^2}{2\pi}\left[-2+\left(\frac{2k_F^2+\lambda^2}{2k_F^2}\right)\ln\left(\frac{4k_F^2+\lambda^2}{\lambda^2}\right)\right], \tag{B3}$$

$$\Sigma''(k_F)=\frac{e^2}{2\pi k_F}\left[2+\left(\frac{4k_F^2+2\lambda^2}{4k_F^2+\lambda^2}\right)\right.$$
$$\left.-\left(\frac{k_F^2+\lambda^2}{k_F^2}\right)\ln\left(\frac{4k_F^2+\lambda^2}{\lambda^2}\right)\right], \tag{B4}$$

and finally

$$\Sigma'''(k_F)=\frac{3e^2}{2\pi k_F^2}\left[-\frac{5}{3}+\left(\frac{k_F^2+\lambda^2}{k_F^2}\right)\ln\left(\frac{4k_F^2+\lambda^2}{\lambda^2}\right)\right.$$
$$\left.-\frac{40k_F^4+42k_F^2\lambda^2+7\lambda^4}{3(4k_F^2+\lambda^2)^2}-\frac{2k_F^2}{3\lambda^2}\right]. \tag{B5}$$

We also require the derivative with respect to k_F of $\mu(k_F)$,

$$\frac{d}{dk_F}\,\mu(k_F)=\mu'(k_F)=\frac{\hbar^2k_F}{m}$$
$$-\frac{e^2}{m}\left[1-\frac{\lambda 2}{4k_F^2}\ln\left(\frac{4k_F^2+\lambda^2}{\lambda^2}\right)\right] \tag{B6}$$

from Eq. (B2). The vertex function and its first two derivatives are also required at $p=k_F$ in the evaluation of Eq. (24). These can be obtained directly from Eq. (26). The result is found to be

$$\Lambda(p)=1+\frac{e^2}{2\pi\mu'(k_F)}\,\frac{k_F}{p}\ln\left(\frac{(p+k_F)^2+\lambda^2}{(p-k_F)^2+\lambda^2}\right). \tag{B7}$$

Setting $p=k_F$, we have

$$\Lambda(k_F)=1+\frac{e^2}{2\pi\mu'(k_F)}\ln\left(\frac{4k_F^2+\lambda^2}{\lambda^2}\right). \tag{B8}$$

The required derivatives of Eq. (B7) are given by

$$\Lambda'(k_F)=\frac{e^2}{2\pi k_F\mu'(k_F)}\left[\frac{4k_F^2}{4k_F^2+\lambda^2}-\ln\left(\frac{4k_F^2+\lambda^2}{\lambda^2}\right)\right] \tag{B9}$$

and

$$\Lambda''(k_F)=\frac{e^2}{\pi k_F\mu'(k_F)}\left[-\frac{20k_F^4+3k_F^2\lambda^2}{(4k_F^2+\lambda^2)^2}\right.$$
$$\left.+\ln\left(\frac{4k_F^2+\lambda^2}{\lambda^2}\right)-\frac{k_F^2}{\lambda^2}\right]. \tag{B10}$$

Inserting these results for $E'(k_F)$, $E''(k_F)$, $E'''(k_F)$, $\Lambda(k_F)$, $\Lambda'(k_F)$, and $\Lambda''(k_F)$ into Eq. (24) yields, after some algebra, the following convenient dimensionless form:

$$4\pi e^2b=\frac{-e^4}{18\pi^2[\mu'(k_F)]^2}\,(A+B)\ , \tag{B11}$$

where

$$A=5+\left(\frac{k_F^2-2\lambda^2}{k_F^2}\right)\ln\left(\frac{4k_F^2+\lambda^2}{\lambda^2}\right)$$
$$-\frac{64k_F^4-4k_F^2\lambda^2-3\lambda^4}{(4k_F^2+\lambda^2)^2}-8\pi k_F a_0 \tag{B12}$$

and

$$B=\frac{\{2\pi k_F a_0+2+2\lambda^2/(4k_F^2+\lambda^2)-(\lambda^2/k_F^2)\ln[(4k_F^2+\lambda^2)/\lambda^2]\}^2}{2\pi k_F a_0-2+[(2k_F^2+\lambda^2)/2k_F^2]\ln[(4k_F^2+\lambda^2)/\lambda^2]}, \tag{B13}$$

where $a_0=\hbar^2/me^2$ is the usual Bohr radius.

Eqs. (B11), (B12), and (B13) complete our derivation for b from the graphs in Fig. 1 for a Yukawa interaction in a fully self-consistent Hartree-Fock approximation.

APPENDIX C

From Eqs. (49) and (41) we can write b' as

$$b'=\frac{-1}{m}\,\frac{\partial}{\partial\mu_0}\,\mathrm{tr}_{p'}\left\{V^{-}(p')\,\mathrm{tr}_p\left[G_0(p'+p)\left(-\frac{1}{2}\,\frac{\partial^2}{\partial\mu_0^2}\,G_0(p)\right.\right.\right.$$
$$\left.\left.\left.+\tfrac{1}{9}\epsilon_{\vec{p}}\,\frac{\partial^3}{\partial\mu_0^3}\,G(p)\right)\right]\right\} \tag{C1}$$

(where we have set $\hbar=1$). Following MB we define

$$I_1(p')=\mathrm{tr}_p\left(G_0(p+p')\,\frac{\partial^2}{\partial\mu_0^2}\,G_0(p)\right)\ , \tag{C2}$$

$$I_2(p')=\mathrm{tr}_p\left(G_0(p+p')\,\frac{\partial^3}{\partial\mu_0^3}\,G_0(p)\right)\ , \tag{C3}$$

and

$$I_3(p')=\mathrm{tr}_p\left(G_0(p+p')\,\epsilon_{\vec{p}}\,\frac{\partial^3}{\partial\mu_0^3}\,G_0(p')\right)\ , \tag{C4}$$

then

$$b'=-\frac{1}{m}\,\frac{\partial}{\partial\mu_0}\,\mathrm{tr}_{p'}\,\{V^{-}(p')[-\tfrac{1}{2}I_1(p')+\tfrac{1}{9}I_3(p')]\}\ . \tag{C5}$$

The forms for $I_1(p')$, $I_2(p')$, and $I_3(p')$ are given by (see MB)

$$I_1(p')=\frac{1}{2}\left(\frac{\partial}{\partial p_0'}\right)^2F^0(p')-\frac{1}{2}\,\frac{\partial}{\partial p_0'}\,\frac{\partial}{\partial\mu_0}\,J(p')$$
$$+\frac{1}{4}\left(\frac{\partial}{\partial\mu_0}\right)^2F^0(p')-2\pi i\delta(p_0')\,S(|\vec{p}'|)\ , \tag{C6}$$

$$I_2(p')=\frac{\partial}{\partial\mu_0}\left[\frac{3}{4}\left(\frac{\partial}{\partial p_0'}\right)^2F^0(p')-\frac{3}{4}\,\frac{\partial}{\partial p_0'}\,\frac{\partial}{\partial\mu_0}\,J(p')\right.$$
$$\left.+\frac{1}{4}\left(\frac{\partial}{\partial\mu_0}\right)^2F^0(p')-3\pi i\delta(p_0')\,S(|\vec{p}'|)\right]\ , \tag{C7}$$

and

$$I_3(p')=\frac{p_0'}{4}\left(\frac{\partial}{\partial p_0'}\right)^3F^0(p')+\frac{3}{4}\left[\left(\frac{\partial}{\partial p_0'}\right)^2F^0(p')\right.$$
$$\left.-\frac{\partial}{\partial p_0'}\,\frac{\partial}{\partial\mu_0}J(p')\right]+\frac{1}{2}\left(\frac{\partial}{\partial\mu_0}\right)^2F^0(p')$$
$$-4\pi i\delta(p_0')\,S(|\vec{p}'|)+\mu_0I_2(p')\ , \tag{C8}$$

where

$$S(|\vec{p}'|)=(m^2/2\pi^2|\vec{p}'|)f(\tfrac{1}{4}\epsilon_{\vec{p}'})\ .$$

To evaluate the above functions we need the various derivatives of the following two functions, $F^0(p')$ and $(\partial J/\partial\mu_0)(p')$, given by

$$F^0(p') = -2\int \frac{d^3p}{(2\pi)^3}\,\frac{f(\epsilon_{\vec{p}+\vec{p}'})-f(\epsilon_{\vec{p}})}{p_0' - \epsilon_{\vec{p}+\vec{p}'} + \epsilon_{\vec{p}} + i\delta\,\mathrm{sgn}p_0'} \tag{C9}$$

and

$$\frac{\partial J}{\partial\mu_0}(p') = 2\int \frac{d^3p}{(2\pi)^3}\,\frac{\delta(\epsilon_{\vec{p}+\vec{p}'}-\mu_0)+\delta(\epsilon_{\vec{p}}-\mu_0)}{p_0' - \epsilon_{\vec{p}+\vec{p}'} + \epsilon_{\vec{p}} + i\delta\,\mathrm{sgn}\,p_0'} \tag{C10}$$

or

$$\begin{aligned} F^0(p') = \frac{-m}{2\pi^2}\,\frac{1}{|\vec{p}'|}\Bigg[&\frac{|\vec{p}'|^2k_F^2 - m^2\alpha^{-2}}{2|\vec{p}'|^2} \\ &\times\ln\left(\frac{\alpha^- - |\vec{p}'|k_F/m + i\delta}{-\alpha^- - |\vec{p}'|k_F/m + i\delta}\right) + \frac{|\vec{p}'|^2k_F^2 - m^2\alpha^{+2}}{2|\vec{p}'|^2} \\ &\times\ln\left(\frac{-\alpha^+ - |\vec{p}'|k_F/m + i\delta}{\alpha^+ - |\vec{p}'|k_F/m + i\delta}\right) + mp_0'\ln\left(\frac{-p_0' + i\delta}{p_0' + i\delta}\right) \\ &+ |\vec{p}'|k_F\Bigg]. \end{aligned} \tag{C11}$$

For $|\vec{p}'| < 2k_F$,

$$\begin{aligned} F^0(p') = \frac{-m}{2\pi^2}\,\frac{1}{|\vec{p}'|}\Bigg[&\frac{|\vec{p}'|^2k_F^2 - m^2\alpha^{-2}}{2|\vec{p}'|^2} \\ &\times\ln\left(\frac{\alpha^- - |\vec{p}'|k_F/m + i\delta}{\alpha^- + |\vec{p}'|k_F/m + i\delta}\right) + \frac{|\vec{p}'|^2k_F^2 - m^2\alpha^{+2}}{2|\vec{p}'|^2} \\ &\times\ln\left(\frac{\alpha^+ + |\vec{p}'|k_F/m - i\delta}{\alpha^+ - |\vec{p}'|k_F/m - i\delta}\right) + |\vec{p}'|k_F\Bigg]. \end{aligned} \tag{C12}$$

For $|\vec{p}'| > 2k_F$, where

$$\alpha^+ = p_0' + \frac{|\vec{p}'|^2}{2m};\quad \alpha^- = p_0' - \frac{|\vec{p}'|^2}{2m},$$

$$\begin{aligned} \frac{\partial J}{\partial\mu_0}(p') = \frac{1}{2\pi^2}\,\frac{m^2}{|\vec{p}'|}\Bigg[&\ln\left(\frac{\alpha^+ + |\vec{p}'|k_F/m - i\delta}{\alpha^+ - |\vec{p}'|k_F/m + i\delta}\right) \\ &- \ln\left(\frac{\alpha^- - |\vec{p}'|k_F/m + i\delta}{\alpha^- + |\vec{p}'|k_F/m - i\delta}\right) + 2\ln\left(\frac{p_0' + i\delta}{p_0' - i\delta}\right)\Bigg]. \end{aligned} \tag{C13}$$

For $|\vec{p}'| < 2k_F$,

$$\begin{aligned} \frac{\partial J}{\partial\mu_0}(p') = \frac{1}{2\pi^2}\,\frac{m^2}{|\vec{p}'|}\Bigg[&\ln\left(\frac{\alpha^+ + |\vec{p}'|k_F/m - i\delta}{\alpha^+ - |\vec{p}'|k_F/m - i\delta}\right) \\ &- \ln\left(\frac{\alpha^- - |\vec{p}'|k_F/m + i\delta}{\alpha^- + |\vec{p}'|k_F/m + i\delta}\right)\Bigg];\quad |\vec{p}'| > 2k_F. \end{aligned} \tag{C14}$$

After a considerable amount of manipulation with various derivatives of $F^0(p')$ and $(\partial/\partial\mu_0)J(p')$, we get

$$I_1(q) = \frac{m^3}{8k_F^3\pi^2q^2}\left[\frac{(1-2q^2)(-y^2+q^2-1)-2y^2(2q^2+1)}{(y^2+1-q^2)^2+4y^2q^2} + \frac{1}{4}\,\frac{1}{q}\ln\left(\frac{y^2+(q+1)^2}{y^2+(q-1)^2}\right)\right], \tag{C15}$$

$$\begin{aligned} I_2(q) = {}&\frac{m^4}{8\pi^2k_F^5q^2}\left(\frac{(3+2q^2)(-y^2+q^2-1)+4q^2y^2}{(y^2+1-q^2)^2+4y^2q^2} + \frac{(3-4q^2)[(y^2+1-q^2)^2-4q^2y^2]+16y^2(y^2+1-q^2)(\frac{3}{4}+q^2)}{[(y^2+1-q^2)^2-4y^2q^2]^2+16q^2y^2(y^2+1-q^2)^2}\right) \\ &+ \frac{im^3}{16\pi k_F^2}\,\delta(p_0')\delta(|\vec{p}'|-2k_F), \end{aligned} \tag{C16}$$

$$\begin{aligned} I_3(q) = {}&\frac{m^3}{4\pi^2k_F^3q^2}\left[\frac{(\frac{3}{4}-2q^2)(-y^2+q^2-1)-2y^2(\frac{5}{4}+2q^2)}{(y^2+1-q^2)^2+4y^2q^2} + \frac{y^2[4y^2q^2-(y^2+1-q^2)^2+2(y^2+1-q^2)(y^2-q^2)]}{[(y^2+1-q^2)^2-4y^2q^2]^2+16y^2q^2(y^2+1-q^2)^2}\right. \\ &\left.+\frac{3}{16}\,\frac{1}{q}\ln\left(\frac{y^2+(q+1)^2}{y^2+(q-1)^2}\right)\right] + \mu_0I_2(q), \end{aligned} \tag{C17}$$

where we have rotated our functions to the imaginary axis and transformed to unitless quantities, i.e.,

$$p_0' = \frac{2k_F^2qyi}{m};\quad q = |\vec{p}'|/2k_F. \tag{C18}$$

Combining Eqs. (C5), (C15), and (C17) we get

$$\begin{aligned} b' = -\frac{2e^2m}{\pi^4}\lim_{q_{\min}\to 0}\frac{\partial}{\partial\mu_0}\int_{q_{\min}/2k_F}^{\infty}\frac{dq}{q} \\ \times\int_0^\infty dy\left(\frac{1}{\epsilon(q,y)}-1\right)F(q,y) - \frac{e^4m^3}{144\pi^4k_F^3}\left(1+\frac{\alpha r_s}{2\pi}\right)^{-2} \end{aligned} \tag{C19}$$

where

$$\epsilon(q,y) = 1 + \frac{\alpha r_s}{4\pi q^2}\,Q(q,y) \tag{C20}$$

and $Q(q,y)$ and $F(q,y)$ are defined in Eqs. (55) and (58). The limiting procedure in Eq. (C19) is required since the integral (without differentiation with respect to μ_0) diverges for small q.

Finally, from Eq. (C19) we get the expression for b' in Eq. (59).

APPENDIX D

From Eq. (51) and Eqs. (C2), (C3), and (C4), $b_2^{(3)}$ can be written

$$b_2^{(3)} = -\frac{1}{m}\mathrm{tr}_{p'}\left[\left(\frac{4\pi e^2}{|\vec{p}'|^2}\,\frac{\partial}{\partial\mu_0}\,\frac{1}{\epsilon(p')}\right)\times\left[-\tfrac{1}{2}I_1(p') + (1/9)\,I_3(p')\right]\right]. \tag{D1}$$

Therefore, the evaluation of $b_2^{(3)}$ is similar to that of b', with an additional term $\partial F^0/\partial\mu_0$ coming from $(\partial/\partial\mu_0)[1/\epsilon(p')]$.

From Eqs. (C11) and (C12) and after rotation to the imaginary axis this term is given by

$$\frac{\partial F^0}{\partial \mu_0} = -\frac{m^2}{4\pi^2 k_F}\frac{1}{q}\ln\left(\frac{y^2+(q+1)^2}{y^2+(q-1)^2}\right), \qquad \text{(D2)}$$

where again $p_0' = 2k_F^2 qyi/m$ and $q = |\vec{p}'|/2k_F$. With $I_1(q)$ and $I_3(q)$ given in Eqs. (C15) and (C17), we finally get

$$b_2^{(3)} = +\frac{e^4}{2\pi^5}\left(\frac{1}{\hbar v_0}\right)^3 \int_0^\infty dq \int_0^\infty dy\, \frac{g(q,y)F(q,y)}{[\tilde{\epsilon}(q,y)]^2}\,. \qquad \text{(D3)}$$

The high-density limit of Eq. (D3) is obtained by using Eqs. (54)–(58) and reduces to Eq. (52).

The difference between b' and $b_2^{(3)}$ is due to the additional contribution from $\partial F^0/\partial\mu_0$. A careful analysis of Eq. (D3) shows that this additional contribution [i.e., $g(q,y)$] enhances the singularity at $q=1$ such that the integrand of q [i.e., after integrating Eq. (D3) over y] behaves like $1/|q-1|$. This singularity is of course removed when the contributions of $b^{(1)}$ and $b^{(2)}$ are added. It again emphasizes the importance of proper grouping of the graphs to all orders (see Sec. V).

Note added in proof: Finally it should be pointed out that the purpose of this discussion has only been to illustrate the singular nature of $b_2^{(3)}$. In a complete evaluation of Eq. (B1), contributions owing to the zero-frequency singularities in the integral must be extracted before the contour rotation.

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[1] P. Hohenberg and W. Kohn, Phys. Rev. 136, B 864 (1964).

[2] W. Kohn and L. J. Sham, Phys. Rev. 140, A 1133 (1965).

[3] L. J. Sham and W. Kohn, Phys. Rev. 145, 561 (1966).

[4] J. R. Smith, J. Phys. C 6, L433 (1973).

[5] J. R. Smith, Phys. Rev. Lett. 25, 1023 (1970).

[6] J. R. Smith, S. C. Ying and W. Kohn, Phys. Rev. Lett. 30, 610 (1973).

[7] W. Kohn (private communication).

[8] L. M. Sander, H. B. Shore, and L. J. Sham, Phys. Rev. Lett. 31, 533 (1973).

[9] L. T. Reinecke and S. C. Ying, Solid State Commun. 14, 381 (1973).

[10] H. Buttner and E. Gerlach, J. Phys. C 6, L433 (1973).

[11] S. Ma and K. Brueckner, Phys. Rev. 165, 18 (1968).

[12] L. J. Sham, in *Computational Methods in Band Theory*, edited by P. M. Marcus, J. F. Janak, and A. R. Williams (Plenum, New York, 1971), p. 458.

[13] F. Herman, J. P. van Dyke, and I. B. Ortenburger, Phys. Rev. Lett. 22, 807 (1969).

[14] I. B. Ortenburger and F. Herman, in *Computational Methods in Band Theory*, edited by P. M. Marcus, J. F. Janak and A. R. Williams (Plenum, New York, 1971), p. 469.

[15] D. J. W. Geldart and M. Rasolt, report (unpublished). Copies available from Dr. Roger Taylor, National Research Council, Ottawa, Canada.

[16] D. J. W. Geldart, M. Rasolt and C. O. Ambladh, Solid State Commun. 16, 243 (1975).

[17] L. Kleinman, Phys. Rev. B 10, 2221 (1974).

[18] The separation of exchange and correlation contribution can be made, in the high-density limit, provided the Coulomb interaction is replaced by $4\pi e^2/\vec{p}+\lambda^2)$ and the $e^2 \to 0$ limit is taken before the $\lambda \to \sigma$ limit (see Sec. III).

[19] B. Y. Tong and L. J. Sham, Phys. Rev. 144, 1 (1966).

[20] N. D. Lang and L. J. Sham, Solid State Commun. (to be published).

[21] B. Y. Tong, Phys. Rev. 4, 1375 (1971).

[22] M. Rasolt and D. J. W. Geldart, Phys. Rev. Lett. 35, 1234 (1975).

[23] M. Rasolt and D. J. W. Geldart, Solid State Commun. (to be published).

[24] P. Nozières and J. M. Luttinger, Phys. Rev. Lett. 127, 1423 (1962).

[25] D. J. W. Geldart and S. H. Vosko, Can. J. Phys. 44, 2137 (1966).

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

[27] L. Hedin and S. Lundqvist, in *Solid State Physics* edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic, New York, 1969), Vol. 23, p. 1.

[28] D. J. W. Geldart, M. Rasolt, J. H. Rose, and H. B. Shore (unpublished).

[29] N. D. Lang and W. Kohn, Phys. Rev. B 1, 4555 (1970).

[30] It should be pointed out that application of these results to surface problems requires that the continuum contribution to B_{xc} dominate those arising from discrete surface states.

[31] M. Gell-Mann and K. A. Brueckner, Phys. Rev. 106, 364 (1957).