

Properties of the electron-hole liquid beyond the local density approximation

M. Rasolt*

*Battelle Columbus Laboratories, Columbus, Ohio 43201
and Department of Physics, Ohio State University, Columbus, Ohio 43210*

D. J. W. Geldart†

*Department of Physics, Dalhousie University, Halifax, Canada B3H 3J5
(Received 28 April 1976)*

An exact evaluation is given in the high-density limit of the first gradient coefficient which enters the exchange plus correlation energy in the Hohenberg-Kohn-Sham formalism for an inhomogeneous two-component (electron-hole) system. Numerical results are given for isotropic electron and hole bands for a range of values of the electron-hole mass and density ratios. An application is made to Ge under [111] strain and the surface energy is calculated in a simple model.

I. INTRODUCTION

The consideration of the electron-hole liquid (EHL) in semiconductors such as Ge and Si has been a subject of much recent interest.¹⁻¹⁰ Although most of the initial works involved the study of EHL in its uniform state, more recently a great effort has gone into extension of EHL to its non-uniform structure. The motivation of studying the inhomogeneous EHL is largely due to the fact that the initial condensation is into finite droplets. Thus the understanding of this transition automatically entails a study of its inhomogeneous character with particular interest to its surface properties (e.g., surface energies or surface tension).

To study such a system, the application of the functional-density formalism^{11,12} generalized to multicomponent systems is particularly useful. Such a generalization is straightforward and rigorous. The results are simply that the energy of such a two-component EHL is now a unique functional of the electron density $n_1(\vec{r})$ and hole density $n_2(\vec{r})$ represented by $E[n_1(\vec{r}), n_2(\vec{r})]$ (the subscripts 1 and 2 will correspond to electrons and holes, respectively). Second, $E[n_1(\vec{r}), n_2(\vec{r})]$ reaches its minimum when the densities $n_1(\vec{r})$ and $n_2(\vec{r})$ correspond to those actually included by applied external potentials $V_1(\vec{r})$ and $V_2(\vec{r})$ (V_1 and V_2 couple to the electrons and holes, respectively).

We can next decompose $E[n_1(\vec{r}), n_2(\vec{r})]$ into the usual electrostatic contribution

$$E_H[n_1(\vec{r}), n_2(\vec{r})] \\ \equiv \frac{e^2}{2K} \int d\vec{r} d\vec{r}' \frac{[n_1(\vec{r}) - n_2(\vec{r})][n_1(\vec{r}') - n_2(\vec{r}')] }{|\vec{r} - \vec{r}'|} \\ + \int d\vec{r} [V_1(\vec{r})n_1(\vec{r}) + V_2(\vec{r})n_2(\vec{r})], \quad (1)$$

the kinetic energy of a noninteracting EHL of den-

sity $n_1(\vec{r})$ and $n_2(\vec{r})$ given by $T_s[n_1(\vec{r}), n_2(\vec{r})]$ and an exchange and correlation term $E^{xc}[n_1(\vec{r}), n_2(\vec{r})]$. Thus $E[n_1(\vec{r}), n_2(\vec{r})]$ is given by

$$E[n_1(\vec{r}), n_2(\vec{r})] \equiv E_H[n_1(\vec{r}), n_2(\vec{r})] \\ + T_s[n_1(\vec{r}), n_2(\vec{r})] + E^{xc}[n_1(\vec{r}), n_2(\vec{r})]. \quad (2)$$

In Eq. (1), K is the static background dielectric constant. We note that Eqs. (1) and (2) can include all band structure effects subject to the approximation that transitions from electron to hole bands are forbidden. Since, for example, in Ge, the recombination times are of the order of 5×10^{-6} sec (because of the indirect gap), such a description is adequate when the system is investigated experimentally for times up to approximately a microsecond.

Although the kinetic energy $T_s[n_1(\vec{r}), n_2(\vec{r})]$ can be approximated as an explicit functional of $n_1(\vec{r})$ and $n_2(\vec{r})$ (see also Sec. IV), Kohn and Sham¹² have formulated a scheme in which $T_s[n_1(\vec{r}), n_2(\vec{r})]$ is written exactly in terms of auxiliary wave functions $\psi(\vec{r})$:

$$T_s[n_1(\vec{r}), n_2(\vec{r})] = -\frac{\hbar^2}{2m_1} \sum_{i=1}^{N_1} \int d\vec{r} \psi_i^{\dagger}(\vec{r}) \nabla^2 \psi_i(\vec{r}) \\ - \frac{\hbar^2}{2m_2} \sum_{j=1}^{N_2} \int d\vec{r} \psi_j^{j*}(\vec{r}) \nabla^2 \psi_j^j(\vec{r}), \quad (3)$$

where N_1 is the number of electrons; N_2 is the number of holes and we have specialized to an isotropic EHL. Although $T_s[n_1(\vec{r}), n_2(\vec{r})]$ is now treated exactly, the price is a much more elaborate procedure for calculating the density and en-

ergy. It is given through the self-consistent solution of the following equations:

$$\left(\frac{-\hbar^2}{2m_1} \nabla^2 + V_1(\vec{r}) + \frac{e^2}{K} \int d\vec{r}' \frac{n_1(\vec{r}') - n_2(\vec{r}')}{|\vec{r} - \vec{r}'|} + v_1^{\text{xc}}[n_1(\vec{r}), n_2(\vec{r})] \right) \psi_1^i(\vec{r}) = \epsilon_1^i \psi_1^i(\vec{r}) \quad (4)$$

and

$$\left(\frac{-\hbar^2}{2m_2} \nabla^2 + V_2(\vec{r}) + e^2 \int d\vec{r}' \frac{n_2(\vec{r}') - n_1(\vec{r}')}{|\vec{r} - \vec{r}'|} + v_2^{\text{xc}}[n_1(\vec{r}), n_2(\vec{r})] \right) \psi_2^i(\vec{r}) = \epsilon_2^i \psi_2^i(\vec{r}), \quad (5)$$

where

$$E^{\text{xc}}[n_1(\vec{r}), n_2(\vec{r})] \approx \int d\vec{r} \{ A^{\text{xc}}[n_1(\vec{r}), n_2(\vec{r})] + B_{11}^{\text{xc}}[n_1(\vec{r}), n_2(\vec{r})] |\nabla n_1(\vec{r})|^2 + B_{22}^{\text{xc}}[n_1(\vec{r}), n_2(\vec{r})] |\nabla n_2(\vec{r})|^2 + O(|\nabla n|^4) \}. \quad (9)$$

Considerable effort has gone into the study of^{7,8} $A^{\text{xc}}[n_1(\vec{r}), n_2(\vec{r})]$ for the uniform EHL. For the nonuniform EHL, the gradient corrections have been found to be important^{9,10,13} as in the case of metallic surface energy calculations.¹⁴⁻¹⁷ Although such corrections have been included within exchange alone⁹ or using the single-component calculation of Ma and Brueckner¹³ (MB), these procedures are inadequate (see Secs. II-IV). Our task, in this work, is to treat these gradient contributions in a much more fundamental way (corresponding to the attention given to A^{xc}).

In Sec. II we give a general formulation for the relation of B_{11}^{xc} , B_{22}^{xc} , and B_{12}^{xc} to the isotropic EHL response functions. In Sec. III we evaluate these quantities in the high-density limit (HDL) for the case of isotropic electron hole bands with arbitrary ratios of electron-hole masses and densities. Since this calculation is restricted to a two-component system, in Sec. IV we apply our results to the case of Ge under a [111] strain.

$$n_\alpha(\vec{r}, t) = -\frac{i}{\hbar} \sum_{\beta=1}^2 \int d\vec{r}' \int_{-\infty}^t dt' \langle O | [\hat{n}_\alpha(\vec{r}, t), \hat{n}_\beta(\vec{r}', t')] | O \rangle V_\beta(\vec{r}', t'). \quad (12)$$

The commutator in Eq. (12) is to be evaluated with the unperturbed ground state $|0\rangle$.

The Fourier transform of Eq. (12) yields

$$n_\alpha(\vec{k}) = -\sum_{\beta=1}^2 \chi_{\alpha\beta}(\vec{k}) V_\beta(\vec{k}), \quad (13)$$

where

$$n_1(\vec{r}) = \sum_{i=1}^{N_1} \psi_1^{i*}(\vec{r}) \psi_1^i(\vec{r}), \quad (6)$$

$$n_2(\vec{r}) = \sum_{j=1}^{N_2} \psi_2^{j*}(\vec{r}) \psi_2^j(\vec{r})$$

and

$$v_1^{\text{xc}}[n_1(\vec{r}), n_2(\vec{r})] = \frac{\delta E^{\text{xc}}}{\delta n_1(\vec{r})} [n_1(\vec{r}), n_2(\vec{r})], \quad (7)$$

$$v_2^{\text{xc}}[n_1(\vec{r}), n_2(\vec{r})] = \frac{\delta E^{\text{xc}}}{\delta n_2(\vec{r})} [n_1(\vec{r}), n_2(\vec{r})]. \quad (8)$$

In this work, our primary interest is to further improve the understanding of the structure of $E^{\text{xc}}[n_1(\vec{r}), n_2(\vec{r})]$. A very appealing approximation for E^{xc} is a gradient expansion in $n_1(\vec{r})$ and $n_2(\vec{r})$, i.e.,

II. FORMULATION

Consider a two-component system of isotropic electron and hole bands in the absence of any external fields. The Hamiltonian for this system is given by

$$H_0 = -\frac{\hbar^2}{2m_1} \sum_{i=1}^{N_1} \nabla_i^2 - \frac{\hbar^2}{2m_2} \sum_{j=1}^{N_2} \nabla_j^2 + \frac{1}{2} \frac{e^2}{K} \sum_{i \neq i'} \frac{1}{|\vec{r}_i - \vec{r}_{i'}|} + \frac{1}{2} \frac{e^2}{K} \sum_{j \neq j'} \frac{1}{|\vec{r}_j - \vec{r}_{j'}|} - \frac{e^2}{K} \sum_{i,j} \frac{1}{|\vec{r}_i - \vec{r}_j|}. \quad (10)$$

Let us next apply weak external fields $V_1(\vec{r}, t)$ and $V_2(\vec{r}, t)$. These external fields will introduce a perturbation on H_0 given by

$$H_I = \sum_{\beta=1}^2 \int d\vec{r} \hat{n}_\beta(\vec{r}) V_\beta(\vec{r}, t), \quad (11)$$

where $\hat{n}_1(\vec{r})$ and $\hat{n}_2(\vec{r})$ are the density operators corresponding to the electrons and holes, respectively.

From linear response, the induced density distributions of both components are given by

$$\chi_{\alpha\beta}(\vec{k}) = \frac{i}{\Omega \hbar} \int_0^\infty dt \langle O | [\hat{n}_\alpha(-\vec{k}, t), \hat{n}_\beta(\vec{k}, 0)] | O \rangle, \quad (14)$$

with Ω being the volume of the system and

$$\hat{n}_\alpha(\vec{k}, t) = \int d\vec{r} e^{i\vec{k} \cdot \vec{r}} \hat{n}_\alpha(\vec{r}, t). \quad (15)$$

In Eq. (13), we have specialized to static external

potentials.

We next write the perturbed ground-state energy to second order in H_I , i.e.,

$$\Delta E = \sum_m \frac{\langle 0 | H_I | m \rangle \langle m | H_I | 0 \rangle}{E_0 - E_m}, \quad (16)$$

$$\begin{aligned} \Delta E(\vec{k}) = & |V_1(\vec{k})|^2 \sum_n \frac{\langle 0 | \hat{n}_1(-\vec{k}) | n \rangle \langle n | \hat{n}_1(\vec{k}) | 0 \rangle}{E_0 - E_n} + |V_2(\vec{k})|^2 \sum_m \frac{\langle 0 | \hat{n}_2(-\vec{k}) | m \rangle \langle m | \hat{n}_2(\vec{k}) | 0 \rangle}{E_0 - E_m} \\ & + \left(V_1(\vec{k}) V_2(-\vec{k}) \sum_l \frac{\langle 0 | \hat{n}_1(-\vec{k}) | l \rangle \langle l | \hat{n}_2(\vec{k}) | 0 \rangle}{E_0 - E_l} + \text{c.c.} \right). \end{aligned} \quad (17)$$

Straightforward spectral decomposition of $\chi_{\alpha\beta}(\vec{k})$ in Eq. (14) allows us to write Eq. (17) as

$$\Delta E(\vec{k}) = -\frac{1}{2} |V_1(\vec{k})|^2 \chi_{11}(\vec{k}) - \frac{1}{2} |V_2(\vec{k})|^2 \chi_{22}(\vec{k}) - |V_1(\vec{k}) V_2(\vec{k})| \chi_{12}(\vec{k}). \quad (18)$$

To relate $\Delta E^{\text{xc}} + \Delta T_s$ in Eq. (2) to Eq. (18), we make use of Eq. (13) and subtract from Eq. (18) the electrostatic contribution of Eq. (1).

The result is

$$\begin{aligned} \Delta E^{\text{xc}}(\vec{k}) + \Delta T_s(\vec{k}) = & \frac{1}{2} \{ [n_1(\vec{k})]^2 \chi_{22}(\vec{k}) + [n_2(\vec{k})]^2 \chi_{11}(\vec{k}) - 2n_1(\vec{k})n_2(\vec{k}) \chi_{12}(\vec{k}) \} / \\ & \{ \chi_{11}(\vec{k}) \chi_{22}(\vec{k}) - [\chi_{12}(\vec{k})]^2 \} - (e^2/K)(2\pi/\vec{k}^2) [n_1(\vec{k}) - n_2(\vec{k})]^2. \end{aligned} \quad (19)$$

Our next task is to convert the χ 's in terms of the irreducible screening functions $\pi_{11}(\vec{k})$, $\pi_{22}(\vec{k})$, and $\pi_{12}(\vec{k})$ [see Fig. 1(a)]. Taking careful consideration of the appropriate signs of the electron-hole interactions we get [see Figs. 1(b)–1(d)]

$$\chi_{11} = [-\pi_{11}(\vec{k}) + (e^2/K)(4\pi/\vec{k}^2)\Delta(\vec{k})]/\epsilon(\vec{k}), \quad (20)$$

$$\chi_{22} = [-\pi_{22}(\vec{k}) + (e^2/K)(4\pi/\vec{k}^2)\Delta(\vec{k})]/\epsilon(\vec{k}), \quad (21)$$

$$\chi_{12} = [-\pi_{12}(\vec{k}) + (e^2/K)(4\pi/\vec{k}^2)\Delta(\vec{k})]/\epsilon(\vec{k}), \quad (22)$$

where

$$\Delta(\vec{k}) = \pi_{11}(\vec{k})\pi_{22}(\vec{k}) - [\pi_{12}(\vec{k})]^2, \quad (23)$$

$$\begin{aligned} \epsilon(\vec{k}) = & 1 + (e^2/K)(4\pi/\vec{k}^2) \\ & \times [-\pi_{11}(\vec{k}) - \pi_{22}(\vec{k}) + 2\pi_{12}(\vec{k})]. \end{aligned} \quad (24)$$

Using Eqs. (20)–(24) in Eq. (19) gives

$$\begin{aligned} \Delta E^{\text{xc}}(\vec{k}) + \Delta T_s(\vec{k}) = & \left\{ -\frac{1}{2} [n_1(\vec{k})]^2 \pi_{22}(\vec{k}) - \frac{1}{2} [n_2(\vec{k})]^2 \pi_{11}(\vec{k}) \right. \\ & \left. + n_1(\vec{k})n_2(\vec{k})\pi_{12}(\vec{k}) \right\} / \Delta(\vec{k}). \end{aligned} \quad (25)$$

To remove the contribution of $\Delta T_s(\vec{k})$ we simply subtract the kinetic energy of the corresponding noninteracting EHL from Eq. (25). This is

$$\Delta T_s(\vec{k}) = -\frac{1}{2} \frac{[n_1(\vec{k})]^2}{\pi_{11}^0(\vec{k})} - \frac{1}{2} \frac{[n_2(\vec{k})]^2}{\pi_{22}^0(\vec{k})}, \quad (26)$$

where

$$\pi_{11}^0(\vec{k}) = -2 \int \frac{d\vec{k}'}{(2\pi)^3} \frac{[f(\vec{k}') - f(\vec{k}' + \vec{k})]}{\hbar^2/2m_1[(\vec{k}' + \vec{k})^2 - \vec{k}'^2]} \quad (27a)$$

and

$$\pi_{22}^0(\vec{k}) = -2 \int \frac{d\vec{k}}{(2\pi)^3} \frac{[f(\vec{k}') - f(\vec{k}' + \vec{k})]}{\hbar^2/2m_2[(\vec{k}' + \vec{k})^2 - \vec{k}'^2]}, \quad (27b)$$

where $|m\rangle$ are the exact eigenstates of H_0 and E_m the corresponding exact eigenvalues.

Restricting our external potentials to a single Fourier component and using Eq. (11), we can rewrite Eq. (16) as

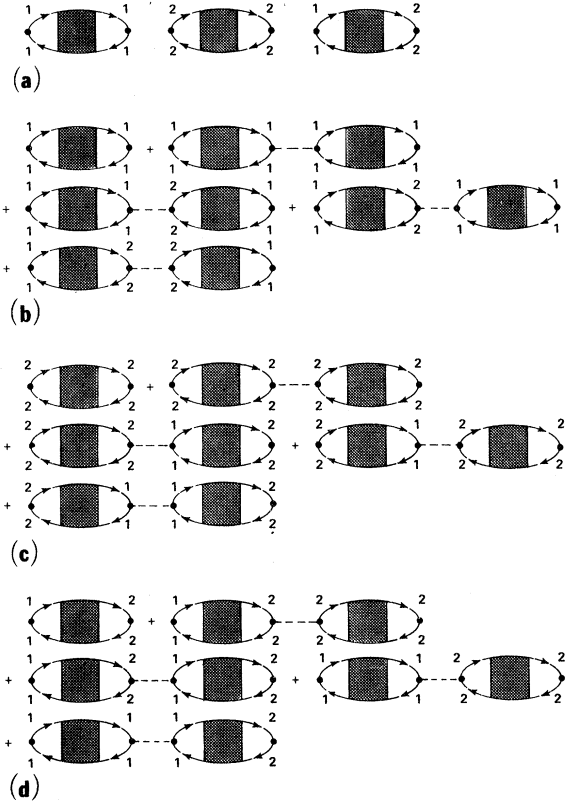


FIG. 1. (a) General form of graphs for the reducible screening function. The lowest-order terms in the decomposition of the reducible screening functions into irreducible screening functions for (b) $\chi_{12}(\vec{k})$; (c) $\chi_{22}(\vec{k})$; and (d) $\chi_{11}(\vec{k})$. The dashed line represents the Coulomb interaction which is repulsive for electron-electron and hole-hole interactions and is attractive for electron-hole interactions.

where $f(\vec{k})$ denotes the usual Fermi occupation function.

Finally, a comparison of Eq. (9) and Eqs. (25) and (26) gives the desired relation between B^{xc} and the irreducible screening functions. B^{xc} is given by the coefficients of the \vec{k}^2 term in the expansion of the following functions:

$$\frac{1}{2} \left(\frac{-\pi_{22}(\vec{k})}{\Delta(\vec{k})} + \frac{1}{\pi_{11}^0(\vec{k})} \right) = \text{const} + B_{11}^{xc} \vec{k}^2 + \dots, \quad (28)$$

$$\frac{1}{2} \left(\frac{-\pi_{11}(\vec{k})}{\Delta(\vec{k})} + \frac{1}{\pi_{22}^0(\vec{k})} \right) = \text{const} + B_{22}^{xc} \vec{k}^2 + \dots, \quad (29)$$

and

$$\pi_{12}(\vec{k})/\Delta(\vec{k}) = \text{const} + B_{12}^{xc} \vec{k}^2 + \dots. \quad (30)$$

In Sec. III, we rigorously evaluate the high-density limit of these irreducible screening functions and the corresponding B_{11}^{xc} , B_{22}^{xc} , and B_{12}^{xc} for an EHL with isotropic bands.

III. EVALUATION OF B^{xc}

From Eqs. (28)–(30), it is apparent that to get B_{11}^{xc} , B_{22}^{xc} , and B_{12}^{xc} requires only the knowledge of $\pi_{11}(\vec{k})$, $\pi_{22}(\vec{k})$, and $\pi_{12}(\vec{k})$ to order \vec{k}^2 . Define then

$$\pi_{11}(\vec{k}) = a_{11}^{-1} + b_{11} \vec{k}^2 + \dots, \quad (31)$$

$$\pi_{22}(\vec{k}) = a_{22}^{-1} + b_{22} \vec{k}^2 + \dots, \quad (32)$$

and

$$\pi_{12}(\vec{k}) = a_{12}^{-1} + b_{12} \vec{k}^2 + \dots. \quad (33)$$

We next observe that the equilibrium density of the uniform EHL corresponds to an effective $r_s \approx 0.63$ and 0.84 for Ge and Si, respectively.⁸ By effective r_s , we mean that lengths are measured in units of the effective Bohr radius given by $a^* = \hbar^2 K / \mu e^2$ so $(a^* r_s)^3 = 3/4\pi n$, where μ is the reduced mass given by $1/\mu = 1/m_1 + 1/m_2$, and n is the density of holes. This high effective density implies that it is adequate to evaluate b_{11} , b_{22} , and b_{12} in the HDL.

The terms corresponding to the HDL of π_{11} , π_{22} , and π_{12} are rigorously given within the random-phase approximation and are displayed in Figs. (2)–(4).

Let us first focus attention on π_{11} and rewrite b_{11} as

$$b_{11} = b_{11}^0 + b_{11}^{ex} + b_{11}^c, \quad (34)$$

where b_{11}^0 is the Lindhard contribution

$$b_{11}^0 = m_1 / 12\pi^2 k_{F1}. \quad (35)$$

(For notational convenience, we set $\hbar = 1$ in the following.) b_{11}^{ex} is the exchange contribution corresponding to Fig. 2(a) and is given by¹⁵

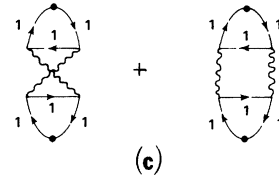
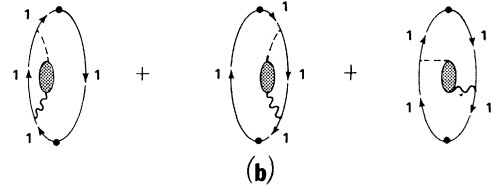
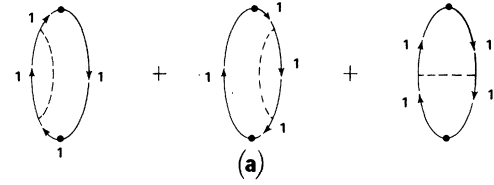


FIG. 2. Lowest-order irreducible graphs contributing to $\chi_{11}(\vec{k})$ in the high-density limit (HDL); (a) bare exchange; (b) screening of exchange graphs; and (c) pure correlation graph not of Hartree-Fock origin.

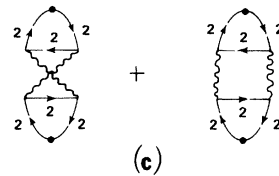
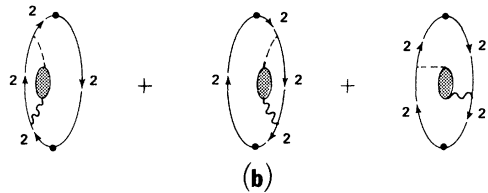
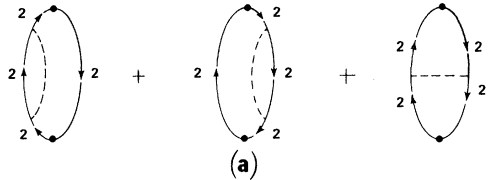


FIG. 3. Lowest-order irreducible graphs contributing to $\chi_{22}(\vec{k})$ in the HDL; (a) bare exchange; (b) screening of exchange graphs; and (c) pure correlation graph not of Hartree-Fock origin.

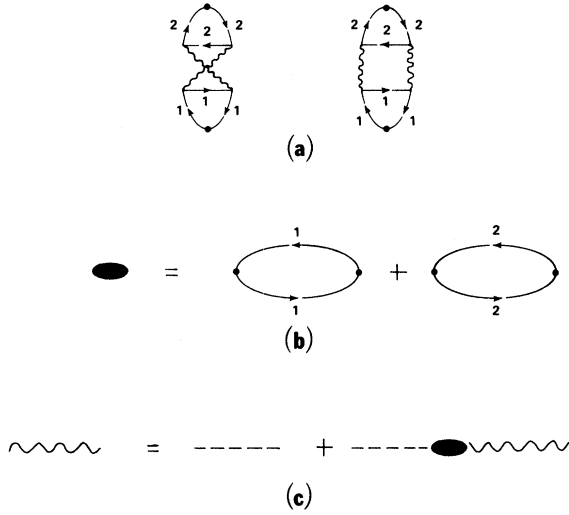


FIG. 4. (a) Lowest-order irreducible graphs contributing to $\chi_{12}(\vec{k})$ in the HDL; (b) the Lindhard screening function; and (c) the lowest-order (random-phase approximation) screened interaction.

$$b_{11}^{\text{ex}} = \frac{5}{72}(e^2/K)m_1^2/\pi^3 k_{F1}^2. \quad (36)$$

The true task of calculating B^{xc} is obviously the correlation contribution b_{11}^c given by Figs. 2(b) and 2(c), with the screened interaction line shown in Figs. 4(b) and 4(c). The calculation of b_{11}^c , however, follows closely that of MB with the main exception being this interaction line. In order to write down the result for b_{11}^c , we briefly outline the main points.

Let us define

$$b_{11}^c = b_{11}^1 + b_{11}^2 + b_{11}^{3,1} + b_{11}^{3,2}, \quad (37)$$

with b_{11}^1 the first two terms in Fig. 2(b), b_{11}^2 the last term in Fig. 2(b), $b_{11}^{3,2}$ that of Fig. 2(c) with $\vec{k} = 0$ in the interaction line, $b_{11}^{3,1}$ the contribution of Fig. 2(c) from the \vec{k} dependence of the interaction lines. Then following the procedures of MB,

$$b_{11}^1 = \frac{1}{m_1} \text{tr}_p \left[\Sigma(p) \left(-\frac{1}{3} \frac{\partial^3}{\partial \mu_1^3} G_0(p) + \frac{1}{9} \epsilon_{\mathfrak{F}} \frac{\partial^4}{\partial \mu_1^4} G_0(p) \right) - \frac{\Sigma(k_{F1}, 0)m_1}{24\pi^2 k_{F1}^3 \mu_1} \right], \quad (38)$$

where

$$\Sigma(p) = -\text{tr}_p[\bar{V}(p')G_0(p+p')], \quad (39)$$

$$\bar{V}(p') = (e^2/K)(4\pi/\bar{p}'^2)[1/\epsilon(p') - 1], \quad (40)$$

$$G_0(p) = [p_0 - \epsilon_{\mathfrak{F}} + \mu_1 + i\delta \text{sgn}(\epsilon_{\mathfrak{F}} - \mu_1)]^{-1}, \quad (41)$$

$$\text{tr}_p(\dots) \equiv \int \frac{d^4p}{(2\pi)^4 i} (\dots), \quad (42)$$

and

$$p \equiv (\vec{p}, p_0), \quad \epsilon_{\mathfrak{F}} = \vec{p}^2/2m_1, \quad \mu_1 = k_{F1}^2/2m_1.$$

All of the above terms enter the MB analysis except that $\epsilon(p')$ is now given by

$$\epsilon(p') = 1 + (e^2/K)(4\pi/\bar{p}'^2)[\pi_1^0(p') + \pi_2^0(p')]. \quad (43)$$

The lowest-order screening functions $\pi_1^0(p')$ and $\pi_2^0(p')$ are the electron and hole bubble graphs given in Fig. 4(b). The difference between $\pi_1^0(p')$ and $\pi_2^0(p')$ is simply the replacement of $m_1 \rightarrow m_2$ and $k_{F1} \rightarrow k_{F2}$. It should be pointed out that although this difference between MB and the present calculation of b_{11}^c for the EHL seems formally minor it does add considerable complexity to the analysis.

Returning to b_{11}^2 and $b_{11}^{3,2}$ we get

$$b_{11}^2 = \frac{1}{m_1} \text{tr}_p \left[\Lambda_p^2 \left(\frac{1}{2} \frac{\partial^2}{\partial \mu_1^2} G_0(p) - \frac{1}{9} \epsilon_{\mathfrak{F}} \frac{\partial^3}{\partial \mu_1^3} G_0(p) \right) \right] \quad (44)$$

and

$$b_{11}^{3,2} = \frac{1}{m_1} \text{tr}_p \left[\Lambda_p^3 \left(\frac{1}{2} \frac{\partial^2}{\partial \mu_1^2} G_0(p) - \frac{1}{9} \epsilon_{\mathfrak{F}} \frac{\partial^3}{\partial \mu_1^3} G_0(p) \right) \right], \quad (45)$$

where Λ_p^2 and Λ_p^3 are the vertex functions shown in Fig. 5. For $b_{11}^{3,1}$ we get

$$b_{11}^{3,1} = -\frac{1}{24} \text{tr}_p \left[\left(\frac{\partial}{\partial \mu_1} \pi_1^0(p) \right)^2 \{ V(p) \nabla_{\mathfrak{F}}^2 V(p) - [\nabla_{\mathfrak{F}} V(p)]^2 \} \right], \quad (46)$$

where

$$V(p) = (e^2/K)(4\pi/\bar{p}^2)[\epsilon(p)]^{-1}. \quad (47)$$

Thus far the analysis has followed closely that of MB with the difference being in the form of $\epsilon(p)$ [Eq. (43)]. We now are forced to depart from MB by using a form of Ward identity applicable to the electron vertex function

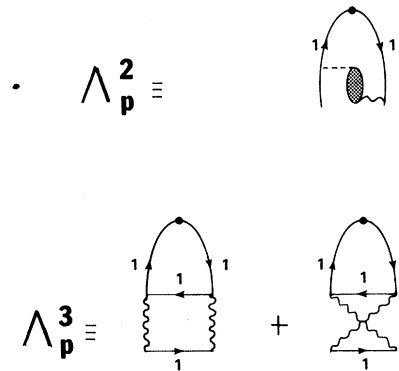


FIG. 5. Lowest-order correlation contributions to the vertex functions.

$$\Lambda^2(p) + \Lambda^3(p) = -\frac{\partial \Sigma(p)}{\partial \mu_1} \quad (48)$$

(i.e., the differentiation is strictly with respect to the electron chemical potential *only*). Using Eqs. (38), (44), (45), and (48), we rewrite

$$b_{11}^1 + b_{11}^2 + b_{11}^{3,2} = b_{11}^1 + b_{11}^{\prime\prime}, \quad (49)$$

where

$$b_{11}^{\prime\prime} = -\frac{1}{m_1} \frac{\partial}{\partial \mu_1} \text{tr}_p \left[\Sigma(p) \left(\frac{1}{2} \frac{\partial^2}{\partial \mu_1^2} G_0(p) - \frac{1}{9} \epsilon_3 \frac{\partial^3}{\partial \mu_1^3} G_0(p) \right) \right] \quad (50)$$

and

$$b_{11}^{\prime\prime} = \frac{1}{6m_1} \text{tr}_p \left(\Sigma(p) \frac{\partial^3}{\partial \mu_1^3} G_0(p) \right). \quad (51)$$

These can next be rewritten in terms of the functions $I_1(p')$, $I_2(p')$, and $I_3(p')$ given by MB,

$$b_{11}^{\prime\prime} = -\frac{1}{m_1} \frac{\partial}{\partial \mu_1} \text{tr}_p \left\{ \bar{V}(p') \left[-\frac{1}{2} I_1(p') + \frac{1}{9} I_3(p') \right] \right\} \quad (52)$$

and

$$b_{11}^{\prime\prime} = -(1/m_1) \text{tr}_p \bar{V}(p') \frac{1}{6} I_2(p'). \quad (53)$$

$$b_{11}^{3,1} = -\frac{e^2}{K} \frac{m_1^2}{\pi^4 k_{F1}^2} \frac{1}{12} \int_0^\infty dy \frac{1}{(y^2+1)^2} \frac{1}{G(\gamma, \beta, y)} \left[-1 + \frac{1}{2} \frac{I(\gamma, \beta, y)}{G(\gamma, \beta, y)} + \frac{1}{6} \left(\frac{I(\gamma, \beta, y)}{G(\gamma, \beta, y)} \right)^2 - \frac{1}{2} \frac{J(\gamma, \beta, y)}{G(\gamma, \beta, y)} \right], \quad (59)$$

where

$$I(\gamma, \beta, y) = -(1+y^2)^{-1} - H(\gamma, \beta, y) \quad (60)$$

and

$$J(\gamma, \beta, y) = -(1+y^2)^{-2} - \gamma\beta [H(\gamma, \beta, y)]^2. \quad (61)$$

In summary, the value of b_{11}^c is the sum of Eqs. (54), (55), and (59). To evaluate b_{22}^c is now trivial. Simple symmetry (Fig. 3) dictates that to get b_{22}^c all we have to do is replace $\gamma \rightarrow 1/\gamma$, $\beta \rightarrow 1/\beta$, $m_1 \rightarrow m_2$, and $k_{F1} \rightarrow k_{F2}$ in Eqs. (54), (55), and (59).

We now turn to b_{12}^c . From Fig. 4(a), we observe that π_{12} has no Lindhard or exchange contributions.

$$b_{12}^{3,2} = -\frac{1}{2m_1} \text{tr}_p \left(\frac{e^2}{K} \frac{4\pi}{\bar{p}^2} \frac{\partial}{\partial \mu_2} \frac{1}{\epsilon(p')} \right) \left[-\frac{1}{2} I_1(p', m_1, k_{F1}) + \frac{1}{9} I_3(p', m_1, k_{F1}) \right] \\ - \frac{1}{2m_2} \text{tr}_p \left(\frac{e^2}{K} \frac{4\pi}{\bar{p}^2} \frac{\partial}{\partial \mu_1} \frac{1}{\epsilon(p')} \right) \left[-\frac{1}{2} I_1(p', m_2, k_{F2}) + \frac{1}{9} I_3(p', m_2, k_{F2}) \right]. \quad (63)$$

The functions $I_1(p', k_{F1}, m_1)$ and $I_3(p', k_{F1}, m_1)$ are identical to those entering Eqs. (52)–(53). The explicit dependence on k_{F1} and m_1 must be stressed since in the second term $k_1 \rightarrow k_{F2}$ and $m_1 \rightarrow m_2$.

Again, after some analysis, the HDL is given by

$$b_{12}^{3,2} = \frac{e^2}{K} \frac{m_1^2}{\pi^4 k_{F1}^2} \frac{1}{72} \frac{\beta^2}{\gamma} \int_0^\infty dy \frac{H(y, \gamma, \beta)}{G(y, \gamma, \beta)} \frac{(9y^4 + 13y^2)}{(y^2+1)^3} + \frac{e^2}{K} \frac{m_2^2}{\pi^4 k_{F2}^2} \frac{1}{72} \left(\beta - \frac{1}{\beta}; \gamma - \frac{1}{\gamma} \right). \quad (64)$$

$b_{12}^{3,1}$ can be seen to be closely related to $b_{11}^{3,1}$. Some simple analysis shows that the only change is to re-

Making the usual substitution, $p' \rightarrow 2k_{F1}q$ and rotating to the imaginary axis $p'_0 \rightarrow (2k_{F1}^2/m_1)qyi$, and after very lengthy analysis we get in the HDL

$$b_{11}^{\prime\prime} = \frac{e^2}{K} \frac{m_1^2}{\pi^4 k_{F1}^2} \frac{1}{36} \int_0^\infty dy \left(1 - \frac{H(\gamma, \beta, y)}{G(\gamma, \beta, y)} \right) \frac{(9y^4 + 13y^2)}{(y^2+1)^3} \quad (54)$$

and

$$b_{11}^{\prime\prime} = \frac{e^2}{K} \frac{m_1^2}{\pi^4 k_{F1}^2} \frac{1}{4} \int_0^\infty dy \ln[G(\gamma, \beta, y)] \frac{y^2(3-y^2)}{(y^2+1)^3}, \quad (55)$$

where

$$G(\gamma, \beta, y) = R(y) + 1/\gamma\beta - y/\gamma^2 \tan^{-1}(\gamma/\beta y), \quad (56)$$

$$R(y) = 1 - y \tan^{-1}(1/y), \quad (57)$$

$$H(\gamma, \beta, y) = (\gamma/\beta^3)(y^2 + \gamma^2/\beta^2)^{-1}, \quad (58)$$

and

$$\gamma = m_1/m_2, \quad \beta = k_{F1}/k_{F2}.$$

The calculation of $b_{11}^{3,1}$ of Eq. (46) is even more tedious. After a considerable amount of manipulation, we get in the HDL

Let us again separate contributions to b_{12}^c by

$$b_{12}^c = b_{12}^{3,1} + b_{12}^{3,2}, \quad (62)$$

where $b_{12}^{3,2}$ is the contribution of Fig. 4(a) with $\vec{k} = 0$ in the interaction lines and $b_{12}^{3,1}$ the contribution of Fig. 4(a) from the \vec{k} dependence of the interaction lines.

Before evaluating $b_{12}^{3,2}$, we note that even for a single component system, treated by MB, this contribution was never separately evaluated but was grouped with other terms. The form for $b_{12}^{3,2}$ is, however, not difficult to derive and is given as follows:

place one of the $\partial\pi_1^0(p)/\partial\mu_1$ in Eq. (46) by $\partial\pi_1^0(p)/\partial\mu_2$, i.e.,

$$b_{12}^{3,1} = -\frac{1}{24} \text{tr} \left[\left(\frac{\partial\pi_1^0}{\partial\mu_1}(p) \frac{\partial\pi_2^0}{\partial\mu_2}(p) \right) \left\{ V(p) \nabla_p^2 V(p) - [\nabla_p V(p)]^2 \right\} \right]. \quad (65)$$

Using Eq. (59) with minor changes to account for $\partial\pi_2^0(p)/\partial\mu_2$ we get in the HDL

$$b_{12}^{3,1} = -\frac{e^2}{K} \frac{m_1^2}{\pi^4 k_{F1}^2} \frac{1}{12} \int_0^\infty \frac{dy}{\beta} \frac{1}{(y^2 + \gamma^2/\beta^2)} \frac{1}{(y^2 + 1)} \frac{1}{G(y, \gamma, \beta)} \left[-1 + \frac{1}{2} \frac{I(y, \gamma, \beta)}{G(y, \gamma, \beta)} + \frac{1}{6} \left(\frac{I(y, \gamma, \beta)}{G(y, \gamma, \beta)} \right)^2 - \frac{1}{2} \frac{J(y, \gamma, \beta)}{G(y, \gamma, \beta)} \right]. \quad (66)$$

In summary, b_{12}^c is thus the sum of Eqs. (64) and (66).

We conclude this section by relating our results for $b^{\text{ex}} + b^c$ to B^{xc} .

It is clear from Eqs. (64) and (66) that $b_{12}^c \sim e^2/K$. Also, $a_{12}^{-1} \sim (e^4/K^2) \ln(e^2/K)$ with the consequence that the HDL result (or equivalently lowest order contributions in e^2/K) given by Eqs. (28)–(30) can be simplified to

$$\frac{1}{2} [-1/\pi_{11}(\vec{k}) + 1/\pi_{11}^0(\vec{k})] = \text{const} + B_{11}^{\text{xc}} \vec{k}^2 + \dots, \quad (67)$$

$$\frac{1}{2} [-1/\pi_{22}(\vec{k}) + 1/\pi_{22}^0(\vec{k})] = \text{const} + B_{22}^{\text{xc}} \vec{k}^2 + \dots, \quad (68)$$

and

$$\pi_{12}(\vec{k})/\pi_{11}(\vec{k})\pi_{22}(\vec{k}) = \text{const} + B_{12}^{\text{xc}} \vec{k}^2 + \dots. \quad (69)$$

Now

$$a_{11} = -\frac{\pi^2}{m_1 k_{F1}} + \frac{e^2}{K} \frac{\pi}{k_{F1}^2} + O \left[\frac{e^4}{K^2} \ln \left(\frac{e^2}{K} \right) \right] \quad (70)$$

and

$$a_{22} = -\frac{\pi^2}{m_2 k_{F2}} + \frac{e^2}{K} \frac{\pi}{k_{F2}^2} + O \left[\frac{e^4}{K^2} \ln \left(\frac{e^2}{K} \right) \right]. \quad (71)$$

We next define the dimensionless quantities Z_{11}^{xc} , Z_{22}^{xc} , Z_{12}^c by

$$\begin{aligned} b_{11}^{\text{xc}} &= (e^2/K) (m_1^2/\pi^4 k_{F1}^2) Z_{11}^{\text{xc}} \\ b_{22}^{\text{xc}} &= (e^2/K) (m_2^2/\pi^4 k_{F2}^2) Z_{22}^{\text{xc}} \end{aligned} \quad (72)$$

and

$$b_{12}^c = (e^2/K) (m_1 m_2 / \pi^4 k_{F1} k_{F2}) Z_{12}^c.$$

Using Eqs. (31)–(33) and (67)–(72), we get

$$B_{11}^{\text{xc}} = \frac{e^2/K}{2k_{F1}^4} (Z_{11}^{\text{xc}} - \frac{1}{6}\pi), \quad (73)$$

$$B_{22}^{\text{xc}} = \frac{e^2/K}{2k_{F2}^4} (Z_{22}^{\text{xc}} - \frac{1}{6}\pi), \quad (74)$$

and

$$B_{12}^{\text{xc}} = \frac{e^2/K}{k_{F1}^2 k_{F2}^2} Z_{12}^c. \quad (75)$$

Finally, we define the dimensionless quantities C_{11}^{xc} , C_{22}^{xc} , C_{12}^{xc} by

$$B_{11}^{\text{xc}} = (e^2/K) C_{11}^{\text{xc}} / n_1^{4/3}, \quad B_{22}^{\text{xc}} = (e^2/K) C_{22}^{\text{xc}} / n_2^{4/3}, \quad (76)$$

and

$$B_{12}^{\text{xc}} = (e^2/K) C_{12}^{\text{xc}} / (n_1 n_2)^{2/3}.$$

Then

$$C_{11}^{\text{xc}} = \frac{1}{2} [1/(3\pi^2)^{4/3}] (Z_{11}^{\text{xc}} - \frac{1}{6}\pi), \quad (77)$$

$$C_{22}^{\text{xc}} = \frac{1}{2} [1/(3\pi^2)^{4/3}] (Z_{22}^{\text{xc}} - \frac{1}{6}\pi), \quad (78)$$

and

$$C_{12}^{\text{xc}} = [1/(3\pi^2)^{4/3}] Z_{12}^c. \quad (79)$$

This completes the first *rigorous* HDL analysis of the gradient terms [Eq. (9)] for an isotropic two-component EHL.

The required integrals for evaluating Z^{xc} and the corresponding C^{xc} have been evaluated numerically and the results are displayed for a range of electron-hole mass ratios γ and for several ratios of densities β in Figs. 6–8. (The β values correspond to $n_1/n_2 = 1$, $n_1/n_2 = \frac{1}{2}$, and $n_1/n_2 = \frac{1}{4}$.) In Sec. IV, we apply these results to Ge under a [111] strain.

IV. APPLICATION TO Ge UNDER [111] STRAIN

In Ge, the electron bands near their minima are ellipsoidal in shape and are localized at the L

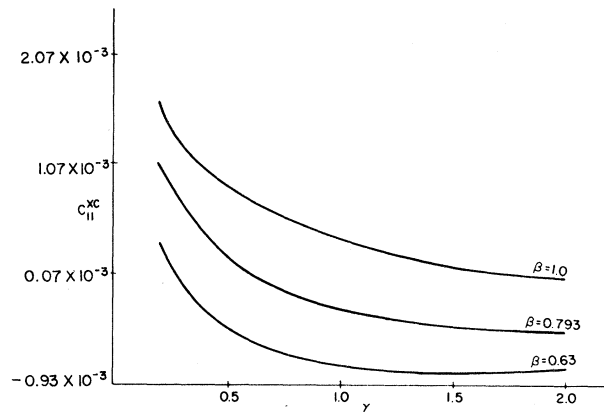


FIG. 6. Calculated HDL electron-electron contribution to the exchange and correlation gradient coefficient (see Sec. III) as a function of electron-hole mass ratio, $\gamma = m_1/m_2$, for electron-hole density ratios of $n_1/n_2 = 1$ (top), $\frac{1}{2}$ (middle), and $\frac{1}{4}$ (lower).

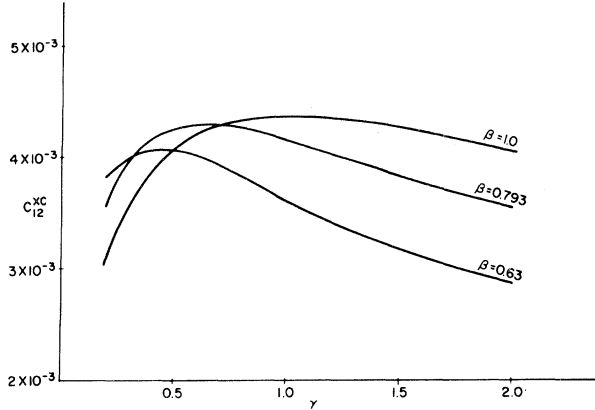


FIG. 7. Calculated HDL hole-hole contribution to the exchange and correlation gradient coefficient (see Sec. III) as a function of the electron-hole mass ratio, $\gamma = m_1/m_2$, for electron-hole density ratios of $n_1/n_2 = 1$ (bottom), $n_1/n_2 = \frac{1}{2}$ (middle), and $n_1/n_2 = \frac{1}{4}$ (top).

point of the zone. There are four equivalent electron ellipsoids. From cyclotron resonance studies, the transverse (m_t) and longitudinal (m_l) masses are known accurately and are $m_t = 0.082m$ and $m_l = 1.58m$,⁸ where m is the free-electron mass.

The hole band structure consists of two bands which are degenerate at Γ . Their dispersion is given by⁸

$$E^*(\vec{k}) = Ak^2 \pm [B^2k^4 + C^2(k_x^2k_y^2 + k_y^2k_z^2 + k_x^2k_z^2)]^{1/2}, \quad (80)$$

where $A = 13.38$, $B = 8.48$, and $C = 13.15$. The dielectric constant for Ge is $K = 15.36$.

In order to apply our former analysis to Ge we are immediately faced with two difficulties. First, the energy bands are highly anisotropic (especial-

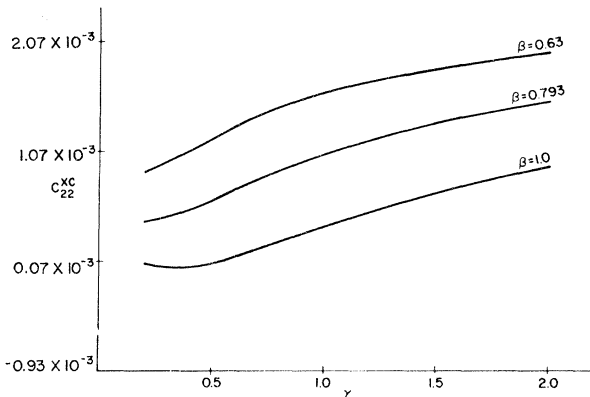


FIG. 8. Calculated HDL electron-hole contribution to the exchange and correlation gradient coefficient (see Sec. III) as a function of the electron-hole mass ratio, $\gamma = m_1/m_2$, for electron hole density ratios of $n_1/n_2 = 1$ ($\beta = 1$), $n_1/n_2 = \frac{1}{2}$ ($\beta = 0.793$), and $n_1/n_2 = \frac{1}{4}$ ($\beta = 0.63$).

ly the electron bands). Second, a full treatment of Ge requires our previous analysis to be generalized from the case of one-electron band and one-hole band to that of four-electron bands and two-hole bands. The latter problem can be avoided by studying Ge under [111] strain. The application of [111] strain to Ge lifts the degeneracy of the two-hole bands and raises the energy of all the other ellipsoids relative to that along the [111] direction. We thus are essentially left with a two-component EHL. As to the former difficulty, we follow Brinkman and Rice⁸ and take the two bands to be isotropic with appropriately chosen effective masses. It is worth noting that in the calculation of $A^{xc}(n_1, n_2)$ [Eq. (9)], the effect of incorporating the anisotropy is to enhance the correlation effects by $\approx 20\%$ for Ge.^{7,8}

The lifting of the degeneracy gives for the hole masses⁸

$$m_t^{-1} = A - \frac{1}{2}(B^2 + \frac{1}{3}C^2)^{1/2} \quad (81)$$

and

$$m_l^{-1} = A + (B^2 + \frac{1}{3}C^2)^{1/2}, \quad (82)$$

which for Ge under strain results in $m_t = 0.04m$ and $m_l = 0.130m$.

To define the appropriate isotropic masses, we recall⁸ that for correlation contributions it is the optical mass (m^{op}) that is appropriate while for the kinetic energy it is the density of states mass (m^d). In terms of m_t and m_l , these are given by⁸ $m^d = (m_t^2 m_l)^{1/3}$ and $(m^{op})^{-1} = \frac{1}{3}(2m_t^{-1} + m_l^{-1})$, respectively. For Ge under [111] strain, we then have $m_1^{op} = 0.12m$, $m_2^{op} = 0.0742m$, with the reduced optical mass $\mu = 0.046m$, while $m_1^d = 0.22m$ and $m_2^d = 0.0878m$ (note that $\gamma = m_1^{op}/m_2^{op} \approx 1.60$).

The first calculation of the surface energy of EHL was carried out by Sander *et al.*⁹ for Ge in a model with four isotropic electron bands and one isotropic hole band. Both kinetic and exchange energies were approximated by making a gradient expansion, i.e., for each component,

$$T_s[n_j] = \int d^3r \{An_j(\vec{r})^{5/3} + C[\nabla n_j(\vec{r})]^2/n_j(\vec{r}) + \dots\} \quad (83)$$

and

$$E_x[n_j] = \int d^3r \{Bn_j(r)^{4/3} + D[\nabla n_j(r)]^2/n_j(r)^{4/3} + \dots\}, \quad (84)$$

where the constants A , B , C , and D are independent of density but are band-structure dependent. The correlation contributions to the energy were neglected. In the case of total charge neutrality, $n_1(r) = n_2(r)$, the total energy functional is express-

ible in terms of the hole density only, which was parametrized in the form

$$n(r) = n_0 / (e^{\alpha x} + 1), \quad (85)$$

where n_0 is the equilibrium density of the bulk EHL and x is the distance normal to the surface. After minimizing with respect to α , the surface energy γ_s can be expressed in terms of n_0 and the parameters in Eqs. (83) and (84) by

$$\gamma_s = 2 |\bar{\mu}| n_0^{2/3} \xi \nu, \quad (86)$$

where $\xi = [\frac{1}{2}(9 - 3 \ln 3 - \sqrt{3}\pi)]^{1/2} \approx 0.36247$, $\bar{\mu}$ is the ground state energy per pair, and

$$\nu = (C/2A - 9D/5B)^{1/2}. \quad (87)$$

Other calculations of the surface properties of the EHL have followed with greater sophistication. Corrections to the anisotropy of the kinetic-energy masses have been included.¹⁸ More recently, the full self-consistent solution of Eqs. (4) and (5) has been carried out for Ge. The upshot is that the surface energy may be adequately treated via a gradient expansion of the kinetic energy. However, those properties which depend sensitively on the energy (such as surface density profile and electrostatic dipole layer) must be calculated in the more complete formalism of Kohn and Sham.¹² In view of the above discussion, and the fact that our main interest at present lies in the correct treatment of the gradient contributions, we will follow the treatment of Sander *et al.*⁹ except that for the case of Ge under [111] strain, we use a model with one isotropic electron band and one isotropic hole band. Of course, correlation contributions to the energy must also be considered.

There are two ways in which correlations play an important role. First, the bulk equilibrium density of electrons (or holes) is more sensitive to correlations than in the case of unstrained Ge (due to the larger kinetic energy). Second, exchange and correlation contributions to *gradient* corrections to the energy are of the same order in e^2/K , even in the HDL, in contrast to the corresponding local density contributions. It is not meaningful to consider only exchange effects. The determination of the bulk density has been studied in some detail^{7,8} and is not our present primary concern so we adopt a simple approach in which the magnitude of the correlation energy is taken into account by the approximation $\epsilon_{\text{ex}} + \epsilon_{\text{corr}} \approx \gamma_{\text{xc}} \epsilon_{\text{ex}}$ where the constant γ_{xc} is determined from the results of Brinkman and Rice⁷ for $r_s \approx 1$ which is the relevant range. Of course, the corresponding gradient contributions to the correlation energy are to be taken from the exact HDL results of Sec. III.

From the above discussion, the approximate total energy functional for the locally neutral EHL can be written

$$E[n] \approx \int d^3r \{ A' n(\vec{r})^{5/3} + B' n(\vec{r})^{4/3} + C' [\nabla n(\vec{r})]^2 / n(\vec{r}) + D' [\nabla n(\vec{r})]^2 / n(\vec{r})^{4/3} \}, \quad (88)$$

where $n(\vec{r})$ is now the hole density and the coefficients in this model are given by the following:

$$A' = \frac{3}{5} (\hbar^2 / 2 \mu_k) \eta^2, \quad (89)$$

where $\mu_k^{-1} = m_{d1}^{-1} + m_{d2}^{-1}$ and $\eta = (3\pi^2)^{4/3}$,

$$B' = -(3/2\pi)(e^2/K)\eta \quad (90)$$

and

$$C' = \hbar^2 / 72 \mu_k. \quad (91)$$

In the absence of correlations, D' would be given by $D' = -7e^2/432\pi\eta K$. Using Eqs. (77)–(79) with $\gamma = 1.60$ and $\beta = 1$, the appropriate contributions including both exchange and correlation are expressible as

$$D' = (e^2/K)(C_{11}^{\text{xc}} + C_{22}^{\text{xc}} + C_{12}^{\text{xc}}), \quad (92)$$

where $C_{11}^{\text{xc}} \approx +0.114 \times 10^{-3}$, $C_{22}^{\text{xc}} \approx 0.7313 \times 10^{-3}$, and $C_{12}^{\text{xc}} \approx 4.238 \times 10^{-3}$, so that $D' = (e^2/K)C^{\text{xc}}$, with $C^{\text{xc}} \approx 5.083 \times 10^{-3}$. Using the density profile of Eq. (85), the minimization of Eq. (88) with respect to α gives Eq. (86) for the surface energy.

At this juncture, it is worth commenting on a point of possible confusion. In Eq. (26) we have written a form for $\Delta T_s(\vec{k})$. The way this quantity is used in subsequent analysis [e.g., Eqs. (28) and (29)], it is clear that the masses entering π_{11} and π_{22} are the optical masses. Thus $T_s(\vec{k})$ is not truly the kinetic energy since the appropriate mass should correspond to the density of states (m^d). Our treatment, however, is correct since we subtract a "pseudo" kinetic energy [$T_s(\vec{k})$] from $E(n)$ and add its correct form (with proper masses) via Eq. (3) or Eq. (83).

Returning to the surface energy calculation, we take $\gamma_{\text{xc}} = \epsilon^{\text{xc}}/\epsilon^{\text{ex}} \approx 1.5$ for $r_s \approx 1$ from the results of Brinkman and Rice.⁸ The α which minimizes the energy is then given by $\alpha^{-1} \approx 0.36\alpha^*$ and the energy per pair is $\bar{\mu} \approx -1.2 \text{ Ry}^*$ where the effective Bohr radius and Rydberg are $a^* \approx 177 \text{ \AA}$ and $\text{Ry}^* \approx 2.65 \text{ meV}$. The effective r_s is $r_s \approx 1.2$ and the surface energy is $\gamma_s \approx 2 \times 10^{-5} \text{ erg cm}^{-2}$. It must be emphasized that the precise values of the bulk parameters are sensitive to the treatment of correlations.^{7,8} For example, taking $\gamma_{\text{xc}} = 1.25$ yields $\bar{\mu} \approx -0.81$ so the stability of the metallic phase relative to free excitons is marginal. However, our primary interest lies in the relative importance of

gradient contributions to the surface energy and firm conclusions concerning this matter *can* be drawn. The first point is that the local density terms and the gradient corrections in Eq. (88) contribute equally to the surface energy in this model. Second, the relative importance of the kinetic energy versus the exchange and correlation contributions to the gradient corrections may be judged by rewriting Eq. (87) as $\nu = (5/216\eta^2 + 6\pi C^{xc}/5\gamma_s^{xc}\eta)^{1/2}$. Again, the kinetic and exchange plus correlation contributions are of the same magnitude. Finally, we turn to the important question of the convergence of the gradient expansion. The kinetic energy can always be treated exactly in the Kohn-Sham formalism so the relevant quantity is the relative contribution to the exchange plus correlation component of the surface energy from the local density term and gradient corrections. The various contributions can

be isolated and it is found that gradient corrections to γ_s^{xc} are about 15% of the local density component of γ_s^{xc} . From the above, we conclude that the convergence of the asymptotic gradient expansion may be adequate for practical purposes and that it is essential to treat correctly the exchange and correlation contributions.

Finally, while there are no measurements (to our knowledge) of the surface energy of Ge under strain, there are several recent measurements¹⁹⁻²¹ for unstrained Ge. To properly treat Ge requires an extension of the above analysis to include the full band structure. The results of such a calculation will be presented elsewhere.

ACKNOWLEDGMENTS

One of us (M. R.) wishes to thank Professor H. B. Shore and Professor J. H. Rose for making their preprint available to us before publication.

*Work supported in part by Battelle Institute Program B 1333-1190.

†Work supported in part by the National Research Council of Canada.

¹L. V. Keldysh, in *Proceedings of the Ninth International Conference on the Physics of Semiconductors* (Nauka, Moscow, 1968), p. 1303.

²V. E. Pokrovskii and K. I. Svistunova, *Pis'ma Zh. Eksp. Teor. Fiz. Pis'ma Red.* **13**, 297 (1971) [*Sov. Phys. -JETP Lett.* **13**, 212 (1971)].

³Y. E. Pokrovskii, *Phys. Status Solidi A* **11**, 385 (1972).

⁴C. Benôit á la Guillaume, M. Voos, and F. Salvan, *Phys. Rev. B* **5**, 3079 (1972); **7**, 1723 (1973).

⁵J. C. Hensel, T. G. Phillips, and T. M. Rice, *Phys. Rev. Lett.* **30**, 227 (1973).

⁶P. H. Handel and C. Kittel, *Proc. Nat. Acad. Sci. USA* **68**, 3120 (1971).

⁷M. Combescot and P. Nozières, *J. Phys. C* **5**, 2369 (1972).

⁸W. F. Brinkman and T. M. Rice, *Phys. Rev. B* **7**, 1508 (1973).

⁹L. M. Sander, H. B. Shore, and L. J. Sham, *Phys. Rev. Lett.* **31**, 533 (1973).

¹⁰H. Büttner and E. Gerlach, *J. Phys. C* **6**, L433 (1973).

¹¹P. Hohenberg and W. Kohn, *Phys. Rev.* **136**, B864 (1964).

¹²W. Kohn and L. J. Sham, *Phys. Rev.* **140**, A1133 (1965).

¹³S. Ma and K. Brueckner, *Phys. Rev.* **165**, 18 (1968).

¹⁴M. Rasolt and D. J. W. Geldart, *Phys. Rev. Lett.* **35**, 1234 (1975).

¹⁵D. J. W. Geldart and M. Rasolt, *Phys. Rev. B* **13**, 1477 (1976).

¹⁶M. Rasolt and D. J. W. Geldart, *Solid State Commun.* **18**, 549 (1976).

¹⁷J. H. Rose, H. B. Shore, D. J. W. Geldart, and M. Rasolt (unpublished).

¹⁸T. L. Reineke and S. C. Ying, *Solid State Commun.* **14**, 381 (1974).

¹⁹B. Etienne, C. Benôit á la Guillaume, and M. Voos, *Phys. Rev. Lett.* **35**, 536 (1975).

²⁰R. M. Westervelt, J. L. Staehli, and E. E. Haller, *Bull. Am. Phys. Soc.* (1976).

²¹B. Etienne, C. Benôit á la Guillaume, and M. Voos, *Bull. Am. Phys. Soc.* (1976).