

Exchange and correlation in the electron gas*

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The theory of Vashishta and Singwi for the dielectric response function is examined. It is shown that in the limit of long wavelength and zero frequency this theory gives the same result as that of Kohn and Sham. The coefficient in the lowest-order gradient expansion for the exchange and correlation energy has been evaluated and compared with the results of others.

I. INTRODUCTION

Attempts to improve upon the dielectric response function of an interacting homogeneous electron gas at metallic densities beyond the random-phase approximation (RPA) have, because of the complexity of the many-body problem, invariably led to several simplifying approximations. Of the several approaches based on mean-field theory that have proved numerically successful, we shall give here particular attention to the recent approach of Vashishta and Singwi¹ (hereafter referred to as VS).

The primary aim of this paper is to examine the basis of the mean-field approach. Starting from an exact quantum-mechanical equation of motion for the density fluctuation in the presence of a weak external field, it will be shown that in the static case and in the limit of long wavelength one obtains an expression for the effective potential, which is identical to the potential obtained in the well-known scheme of Hohenberg, Kohn, and Sham.^{2,3} Based on the latter scheme, Sham⁴ has recently suggested an alternative form of the effective potential. However, he seems to have overlooked the similarity of his approach to that of Vashishta and Singwi, which makes the two potentials the same in the long-wavelength limit. We shall also discuss the numerical values of the coefficients of the lowest-order gradient expansion of the exchange and correlation energy of a slightly inhomogeneous electron gas within the framework of the approximate scheme of VS. We shall further comment on their response function for arbitrary wave vector and frequency.

II. MEAN-FIELD APPROACH

Consider a homogeneous electron gas on a uniform positive background which is perturbed by a weak external potential varying slowly in space and time. The exact quantum-mechanical equation of motion for the density $\langle n(\vec{r}, t) \rangle$ is⁵

$$\frac{\partial^2}{\partial t^2} \langle n(\vec{r}, t) \rangle - \frac{1}{m} \nabla_\alpha \nabla_\beta \Pi_{\alpha\beta}(\vec{r}, t)$$

$$= -\frac{1}{m} \int d\vec{r}' \nabla_\alpha [\nabla_\alpha v(\vec{r} - \vec{r}') \langle n(\vec{r}, t) n(\vec{r}', t) \rangle] \\ = \frac{1}{m} \nabla_\alpha [\langle n(\vec{r}, t) \rangle \nabla_\alpha V_{\text{ext}}(\vec{r}, t)] \quad (1)$$

where ∇_α denotes differentiation with respect to the α th Cartesian component of \vec{r} , and the usual convention of summation over repeated indices is used. The angular brackets denote the ground-state expectation value. The kinetic tensor $\Pi_{\alpha\beta}(\vec{r}, t)$ is defined by

$$\Pi_{\alpha\beta}(\vec{r}, t) = \sum_\sigma \int d\vec{p} \frac{p_\alpha p_\beta}{m} f_\sigma(\vec{p}, \vec{r}, t) \quad (2)$$

where \vec{p} is the momentum, $f_\sigma(\vec{p}, \vec{r}, t)$ is the usual Wigner phase-space distribution function, and σ is the spin index. $v(r)$ is the Coulomb interaction, and $V_{\text{ext}}(\vec{r}, t)$ is the external perturbing potential.

In the event that the external potential varies slowly in space and time, we may assume that $\langle n(\vec{r}, t) n(\vec{r}', t) \rangle$ and $\Pi_{\alpha\beta}(\vec{r}, t)$ have relaxed to their local equilibrium values. In that case, these will depend only on the value of the local density. Therefore,

$$\langle n(\vec{r}, t) n(\vec{r}', t) \rangle \\ = \langle n(\vec{r}, t) \rangle \langle n(\vec{r}', t) \rangle g(\vec{r} - \vec{r}'; \langle n \rangle) \quad (3)$$

and

$$\Pi_{\alpha\beta}(\vec{r}, t) = \frac{2}{3} \delta_{\alpha\beta} t(\langle n \rangle) \quad (4)$$

where $t(\langle n \rangle)$ is the local value of the kinetic-energy density. Equation (3) is the definition of the pair correlation function, which now depends only on $(\vec{r} - \vec{r}')$ and the local density $\langle n \rangle$. We are concerned here with the deviation $\langle \bar{n}(\vec{r}, t) \rangle$ of the density from its unperturbed value n . We have

$$\delta \langle n(\vec{r}, t) n(\vec{r}', t) \rangle = n \left(1 + \frac{n}{2} \frac{\partial}{\partial n} \right) \\ \times g(\vec{r} - \vec{r}'; n) [\langle \bar{n}(\vec{r}, t) \rangle + \langle \bar{n}(\vec{r}', t) \rangle] \quad (5)$$

where we have written

$$\delta g(\vec{r} - \vec{r}'; \langle n \rangle) = \frac{1}{2} \frac{\partial g(\vec{r} - \vec{r}'; n)}{\partial n} \times [\langle \bar{n}(\vec{r}, t) \rangle + \langle \bar{n}(\vec{r}', t) \rangle] , \quad (6)$$

which is certainly true for disturbances varying slowly in space and time. In writing Eq. (6) we have taken notice of the fact that $g(\vec{r} - \vec{r}'; \langle n \rangle)$ is symmetric in \vec{r} and \vec{r}' .

Inserting Eqs. (5) and (4) in Eq. (1), we have, after linearization, the following equation of motion for $\langle \bar{n}(\vec{r}, t) \rangle$:

$$\begin{aligned} \frac{\partial^2}{\partial t^2} \langle \bar{n}(\vec{r}, t) \rangle - \frac{2}{3m} \left(\frac{\partial t}{\partial n} \right) \nabla^2 \langle \bar{n}(\vec{r}, t) \rangle - (n/m) \nabla_\alpha \\ \times \left\{ \int d\vec{r}' \nabla_\alpha v(\vec{r} - \vec{r}') \right. \\ \times \left[\left(1 + \frac{n}{2} \frac{\partial}{\partial n} \right) g(\vec{r} - \vec{r}'; n) \right] \\ \left. \times \langle \bar{n}(\vec{r}', t) \rangle \right\} = \frac{n}{m} \nabla^2 V_{\text{ext}}(\vec{r}, t) . \end{aligned} \quad (7)$$

Defining an effective potential through

$$\begin{aligned} \vec{\nabla} V_{\text{eff}}(\vec{r}, t) = \vec{\nabla} V_H(\vec{r}, t) + \int d\vec{r}' \vec{\nabla} v(\vec{r} - \vec{r}') \\ \times \left(1 + \frac{n}{2} \frac{\partial}{\partial n} \right) [g(\vec{r} - \vec{r}'; n) - 1] \langle \bar{n}(\vec{r}', t) \rangle , \end{aligned} \quad (8)$$

where $V_H(\vec{r}, t)$ is the Hartree potential, Eq. (7) can be written in a compact form as

$$\frac{\partial^2}{\partial t^2} \langle \bar{n}(\vec{r}, t) \rangle - \frac{2}{3m} \left(\frac{\partial t}{\partial n} \right) \nabla^2 \langle \bar{n}(\vec{r}, t) \rangle = \frac{n}{m} \nabla^2 V_{\text{eff}}(\vec{r}, t) . \quad (9)$$

Expanding

$$\langle \bar{n}(\vec{r}', t) \rangle = \langle \bar{n}(\vec{r}, t) \rangle + (\vec{r}' - \vec{r}) \cdot \vec{\nabla} \langle \bar{n}(\vec{r}, t) \rangle + \dots , \quad (10)$$

and using it in Eq. (8), we have for Eq. (9)

$$\begin{aligned} \frac{\partial^2}{\partial t^2} \langle \bar{n}(\vec{r}, t) \rangle - \frac{1}{m} \left[\frac{2}{3} \left(\frac{\partial t}{\partial n} \right) - \frac{n}{3} \int \vec{r} \cdot \vec{\nabla} v(r) \right. \\ \left. \times \left(1 + \frac{n}{2} \frac{\partial}{\partial n} \right) [g(\vec{r}, n) - 1] d\vec{r} \right] \nabla^2 \langle \bar{n}(\vec{r}, t) \rangle \\ = \frac{n}{m} \nabla^2 V_H(\vec{r}, t) . \end{aligned} \quad (11)$$

If p is the static pressure, then it follows from Eq. (11) that

$$\begin{aligned} \frac{\partial p}{\partial n} = \frac{2}{3} \left(\frac{\partial t}{\partial n} \right) - \frac{n}{3} \int r \frac{dv(r)}{dr} \\ \times \left(1 + \frac{n}{2} \frac{\partial}{\partial n} \right) [g(\vec{r}, n) - 1] d\vec{r} \\ = \frac{\partial}{\partial n} \left[\frac{2}{3} t(n) - \frac{n^2}{6} \int r \frac{dv(r)}{dr} \right. \end{aligned}$$

$$\left. \times [g(\vec{r}, n) - 1] d\vec{r} \right\} . \quad (12)$$

The quantity within the curly brackets is the pressure as obtained from the virial theorem. For a static external potential, Eq. (11), on using Eq. (12), becomes

$$\nabla^2 \left[\left(\frac{\partial p}{\partial n} \right) \langle \bar{n}(\vec{r}) \rangle + n V_H(\vec{r}) \right] = 0 \quad (13a)$$

or

$$\left(\frac{\partial p}{\partial n} \right) \langle \bar{n}(\vec{r}) \rangle + n V_H(\vec{r}) = 0 . \quad (13b)$$

The following relation between the kinetic-energy density and the pair distribution function $g(\mathbf{r})$ can be easily established [see Appendix, Eq. (A9)]:

$$\begin{aligned} \frac{5}{3} t(n) - n \frac{\partial t(n)}{\partial n} = \frac{n^2}{2} \int v(r) \left(1 + n \frac{\partial}{\partial n} \right) \\ \times [g(\vec{r}; n) - 1] d\vec{r} + \frac{n^2}{6} \int r \frac{dv(r)}{dr} \\ \times [g(\vec{r}; n) - 1] d\vec{r} . \end{aligned} \quad (14)$$

The solution of Eq. (14) is

$$\begin{aligned} t(n) - t_0(n) = - \frac{n^2}{2} \int v(r) [g(\vec{r}, n) - 1] d\vec{r} \\ - \frac{n^{5/3}}{6} \int v(r) d\vec{r} \int_\infty^n n'^{-2/3} \\ \times [g(\vec{r}, n') - 1] dn' , \end{aligned} \quad (15)$$

where $t_0(n)$ is the kinetic energy density in the non-interacting case. Equation (15) on differentiation yields

$$\begin{aligned} \frac{2}{3n} \frac{\partial}{\partial n} [t(n) - t_0(n)] = - \frac{7}{9} \int v(r) \\ \times [g(\vec{r}, n) - 1] d\vec{r} - \frac{n}{3} \int v(r) \frac{\partial g(\vec{r}; n)}{\partial n} d\vec{r} \\ - \frac{5}{27} n^{-1/3} \int v(r) d\vec{r} \int_\infty^n n'^{-2/3} \\ \times [g(\vec{r}, n') - 1] dn' . \end{aligned} \quad (16)$$

Equation (15) can also be written in the alternative form¹

$$\begin{aligned} \frac{1}{n} [t(n) - t_0(n)] = - \frac{4}{\pi} \left(\frac{9\pi}{4} \right)^{1/3} \\ \times \left(\frac{1}{r_s^2} \int_0^{r_s} \bar{\gamma}(r_s') dr_s' - [\bar{\gamma}(r_s)/r_s] \right) \text{Ry} , \end{aligned} \quad (17)$$

where $\bar{\gamma}(r_s)$ is

$$\begin{aligned} \bar{\gamma}(r_s) = - \left(\frac{9}{4\pi} \right)^{2/3} \left(\frac{1}{12\pi e^2} \right) \frac{1}{a_B^2 r_s^2} \\ \times \int v(r) [g(\vec{r}; n) - 1] d\vec{r} , \end{aligned} \quad (18)$$

a_B being the Bohr radius and $4\pi r_s^3 a_B^3 / 3 = 1/n$.

If we include the interacting part of the kinetic energy in the effective potential in Eq. (9), it can be written as

$$\begin{aligned} \tilde{V}_{\text{eff}}(\vec{r}, t) = & V_H(\vec{r}, t) + \left[-\frac{1}{3} \int r \frac{dv(r)}{dr} \right. \\ & \times \left(1 + \frac{n}{2} \frac{\partial}{\partial n} \right) [g(\vec{r}; n) - 1] d\vec{r} \\ & \left. + \frac{2}{3n} \left(\frac{\partial t_0}{\partial n} - \frac{\partial t_0(n)}{\partial n} \right) \right] \langle \bar{n}(\vec{r}, t) \rangle . \end{aligned} \quad (19)$$

In the scheme of VS, the induced density in the Fourier space is written as

$$\langle \bar{n}(\vec{q}, \omega) \rangle = \chi_0(\vec{q}, \omega) \tilde{V}_{\text{eff}}(\vec{q}, \omega) , \quad (20)$$

where χ_0 is the usual free-electron polarizability, and \tilde{V}_{eff} in ordinary space is

$$\begin{aligned} \tilde{V}_{\text{eff}}(\vec{r}, t) = & V_H(\vec{r}, t) - \frac{1}{3} \int r \frac{dv(r)}{dr} \\ & \times \left(1 + an \frac{\partial}{\partial n} \right) [g(\vec{r}; n) - 1] d\vec{r} . \end{aligned} \quad (21)$$

It was found that, choosing $a = \frac{2}{3}$, the compressibility sum rule was very well satisfied (see Fig. 4 of Ref. 1). It implies that the last term in Eq. (19) is approximated by

$$-\frac{n}{18} \int r \frac{dv(r)}{dr} \frac{\partial}{\partial n} [g(\vec{r}; n)] d\vec{r} .$$

Vaishya and Gupta⁶ checked this approximation using the self-consistent pair correlation of VS, and found it to be exceedingly accurate for r_s values of interest. The VS scheme implies that $\partial p / \partial n$ entering in Eq. (13b) is

$$\begin{aligned} \frac{\partial p}{\partial n} = & \frac{2}{3} \left(\frac{\partial t_0}{\partial n} \right) - \frac{n}{3} \int r \frac{dv(r)}{dr} \\ & \times \left(1 + \frac{2}{3} n \frac{\partial}{\partial n} \right) [g(\vec{r}, n) - 1] d\vec{r} . \end{aligned} \quad (22)$$

We can, therefore, conclude that, for all practical purposes, the VS scheme gives the exact value for the compressibility.

III. KOHN-SHAM APPROACH

Kohn and Sham³ are concerned only with the static situation. They write the ground-state energy in the form:

$$\begin{aligned} E = & T_0 + \frac{1}{2} \int d\vec{r} d\vec{r}' v(\vec{r} - \vec{r}') \langle n(\vec{r}) \rangle \langle n(\vec{r}') \rangle \\ & + \int d\vec{r} \langle n(\vec{r}) \rangle V_{\text{ext}}(\vec{r}) + E_{\text{xc}}[\langle n \rangle] , \end{aligned} \quad (23)$$

where

$$\begin{aligned} E_{\text{xc}}[\langle n \rangle] = & \frac{1}{2} \int d\vec{r} d\vec{r}' v(\vec{r} - \vec{r}') \\ & \times \langle n(\vec{r}) n(\vec{r}') \rangle_c + T[\langle n \rangle] - T_0[\langle n \rangle] . \end{aligned} \quad (24)$$

The suffix c on the expression within angular brackets has the usual meaning of the correlated part of $\langle n(\vec{r}) n(\vec{r}') \rangle$. Kohn and Sham also write Eq. (24) in the form:

$$\begin{aligned} E_{\text{xc}}[\langle n \rangle] = & E_{\text{xc}}(n) + \frac{1}{2} \int d\vec{r} d\vec{r}' \\ & \times K_{\text{xc}}(\vec{r} - \vec{r}'; n) \langle \bar{n}(\vec{r}) \rangle \langle \bar{n}(\vec{r}') \rangle , \end{aligned} \quad (25)$$

which in the long-wavelength limit becomes:

$$E_{\text{xc}}[\langle n \rangle] = E_{\text{xc}}(n) + \frac{1}{2} K_{\text{xc}}(n) \int d\vec{r} \langle \bar{n}(\vec{r}) \rangle^2 , \quad (26)$$

where $K_{\text{xc}}(n) = \int K_{\text{xc}}(\vec{r}; n) d\vec{r}$. Similarly

$$\begin{aligned} T_0[\langle n \rangle] = & T_0(n) + \frac{1}{2} \int d\vec{r} d\vec{r}' \\ & \times K_0(\vec{r} - \vec{r}'; n) \langle \bar{n}(\vec{r}) \rangle \langle \bar{n}(\vec{r}') \rangle , \end{aligned} \quad (27)$$

and

$$T_0[\langle n \rangle] = T_0(n) + \frac{1}{2} K_0(n) \int d\vec{r} \langle \bar{n}(\vec{r}) \rangle^2 \quad (28)$$

in the same limit.

The basic equation of Hohenberg-Kohn-Sham for determining $\langle \bar{n}(\vec{r}) \rangle$ is

$$\frac{\delta T_0[\langle n \rangle]}{\delta \langle \bar{n}(\vec{r}) \rangle} + \frac{\delta E_{\text{xc}}[\langle n \rangle]}{\delta \langle \bar{n}(\vec{r}) \rangle} + V_H(\vec{r}) = 0 , \quad (29)$$

which together with Eqs. (25) and (27) yields

$$\int d\vec{r}' [K_0(\vec{r} - \vec{r}'; n) + K_{\text{xc}}(\vec{r} - \vec{r}'; n)] \langle \bar{n}(\vec{r}') \rangle + V_H(\vec{r}) = 0 , \quad (30)$$

where $V_H(\vec{r})$ is the Hartree potential. For a slowly varying disturbance, Eq. (30) becomes

$$[K_0(n) + K_{\text{xc}}(n)] \langle \bar{n}(\vec{r}) \rangle + V_H(\vec{r}) = 0 , \quad (31)$$

where

$$K_0(n) = \frac{1}{V} \frac{\partial^2 T_0(n)}{\partial n^2} \quad (32)$$

and

$$K_{\text{xc}}(n) = \frac{1}{V} \frac{\partial^2 E_{\text{xc}}(n)}{\partial n^2} , \quad (33)$$

V being the volume.

Now, comparing Eq. (31) with the corresponding equations (13b) and (12) of the mean-field theory we have the following correspondence:

$$K_0(n) \leftrightarrow \frac{2}{3n} \left(\frac{\partial t_0}{\partial n} \right) \quad (34)$$

and

$$K_{xc}(n) \leftrightarrow \frac{2}{3n} \left[\left(\frac{\partial t}{\partial n} \right) - \left(\frac{\partial t_0}{\partial n} \right) \right] - \frac{1}{3} \int r \frac{dv(r)}{dr} \times \left(1 + \frac{n}{2} \frac{\partial}{\partial n} \right) [g(\vec{r}; n) - 1] d\vec{r} . \quad (35)$$

Equation (24) can be written as

$$E_{xc}(n) = \frac{1}{2} V n^2 \int v(r) [g(\vec{r}; n) - 1] d\vec{r} + V [t(n) - t(n_0)] . \quad (36)$$

The exchange and correlation part of the chemical potential, $\mu_{xc}(n)$, is

$$\mu_{xc}(n) \equiv \frac{1}{V} \frac{\partial E_{xc}(n)}{\partial n} = n \int v(r) \left(1 + \frac{n}{2} \frac{\partial}{\partial n} \right) \times [g(\vec{r}; n) - 1] d\vec{r} + \left[\frac{\partial t(n)}{\partial n} - \frac{\partial t_0(n)}{\partial n} \right] \quad (37)$$

and

$$K_{xc}(n) \equiv \frac{\partial \mu_{xc}(n)}{\partial n} = \int v(r) \left(1 + 2n \frac{\partial}{\partial n} + \frac{n^2}{2} \frac{\partial^2}{\partial n^2} \right) \times [g(\vec{r}; n) - 1] d\vec{r} + \left(\frac{\partial^2 t(n)}{\partial n^2} - \frac{\partial^2 t_0(n)}{\partial n^2} \right) . \quad (38)$$

Equations (38) and (35) have to give the same value for $K_{xc}(n)$. And that it is so follows immediately if one makes use of Eq. (14) in Eq. (38). Differentiating Eq. (14) with respect to n we have

$$\frac{2}{3} \left(\frac{\partial t}{\partial n} \right) - \frac{n}{3} \int r \frac{dv(r)}{dr} \left(1 + \frac{n}{2} \frac{\partial}{\partial n} \right) [g(\vec{r}; n) - 1] d\vec{r} = n \left[\left(\frac{\partial^2 t}{\partial n^2} \right) + \int v(r) \left(1 + 2n \frac{\partial}{\partial n} + \frac{n^2}{2} \frac{\partial^2}{\partial n^2} \right) \times [g(\vec{r}; n) - 1] d\vec{r} \right] . \quad (39)$$

For a noninteracting electron gas

$$\frac{2}{3} \left(\frac{\partial t_0}{\partial n} \right) = n \left(\frac{\partial^2 t_0}{\partial n^2} \right) . \quad (40)$$

Using Eqs. (39) and (40) in Eq. (38), we see that Eqs. (38) and (35) are indeed identical.

We have thus established that in the limit of long wavelength and static disturbance (i. e. $\omega = 0$), $K_{xc}(n)$ as obtained from the mean-field approach of VS is identical with that obtained from the Kohn-Sham approach. In the procedure of Vashishta and Singwi $K_{xc}(n)$ is given by

$$K_{xc}(n) = -\frac{1}{3} \int r \frac{dv(r)}{dr} \times \left(1 + an \frac{\partial}{\partial n} \right) [g(\vec{r}; n) - 1] d\vec{r} . \quad (41)$$

with $a = \frac{2}{3}$. As pointed out before, Eq. (41) is for practical purposes as good as the exact one. The VS procedure has the computational advantage in that only first density derivatives enter. Even this

is a considerable complication relative to the earlier procedure,⁷ where no density derivative terms occurs.

IV. STATIC DIELECTRIC FUNCTION

In the mean-field approach the density response function is given by

$$\chi(\vec{q}, \omega) = \frac{\chi_0(\vec{q}, \omega)}{1 - v(q) [1 - G(q)] \chi_0(\vec{q}, \omega)} \quad (42)$$

where $\chi_0(\vec{q}, \omega)$ is the usual Lindhard function, and where the function $G(q)$ in the VS scheme is

$$G(q) = \left(1 + \frac{2}{3} n \frac{\partial}{\partial n} \right) \times \left(-\frac{1}{n} \int \frac{d\vec{q}'}{(2\pi)^3} \frac{\vec{q} \cdot \vec{q}'}{q'^2} [S(\vec{q} - \vec{q}'; n) - 1] \right) , \quad (43)$$

$S(\vec{q}; n)$ being the static structure factor.

The induced density is

$$\langle \bar{n}(\vec{q}, \omega) \rangle = \chi(\vec{q}, \omega) V_{\text{ext}}(\vec{q}, \omega) , \quad (44)$$

which on using Eq. (42) can be rewritten as

$$[-1/\chi_0(\vec{q}, \omega) - v(q) G(q)] \times \langle \bar{n}(\vec{q}, \omega) \rangle + V_H(\vec{q}, \omega) = 0 \quad (45)$$

Comparing the above equation for $\omega = 0$ with the Fourier transform of Eq. (30), we have the following identification:

$$K_0(q) = -1/\chi_0(\vec{q}, 0) \quad (46)$$

and

$$K_{xc}(q) = -v(q) G(q) . \quad (47)$$

Kohn and Sham suggested expanding $K_{xc}(q)$ in powers of q (gradient expansion) but they noted that such an expansion is not appropriate for $K_0(q)$.

Therefore, they reformulated their theory in terms of a Schrödinger equation, where $K_{xc}(r)$ enters as an effective potential and $K_0(r)$ goes over to $-\hbar^2 \nabla^2 / 2m$. This corresponds to using the exact free-particle response function $\chi_0(\vec{q}, 0)$ in the treatment of VS. The difference between the two schemes is, however, that Kohn and Sham can treat nonlinear response in contrast to VS. This is, of course, a very essential aspect of the former procedure.

In the Kohn-Sham procedure $K_{xc}(r)$ is expressed as a functional derivative of $E_{xc}(n)$, which, however, can be directly evaluated only in the long-wavelength limit. On the other hand, in the VS scheme $G(q)$ can be calculated for arbitrary q , although it represents an approximation. In the long-wavelength limit it is exact, as shown before.

Recently Hedin and Lundqvist⁸ have argued that $K_{xc}(q)$ stays approximately constant up to $q \approx 2k_F$. In support of this they cite the close agreement they get with the $G(q)$ of Geldart and Taylor.⁹ This

contention, however, is not supported by the $G(q)$ of Vashishta and Singwi. In the VS scheme $K_{xc}(q)$ stays almost constant up to $q \approx k_F$ and not beyond. The reason Hedin and Lundqvist give for trusting the result of Geldart and Taylor is that the latter gives very good phonon dispersion curves. With the $G(q)$ of VS one obtains equally good phonon dispersion curves.¹⁰ This, therefore, cannot be considered a good test. Another test is to calculate the pair distribution function, since it is sensitive to the form of $G(q)$ over the whole region ranging from $q=0$ to $q \approx 2k_F$. It has been found that most dielectric functions give very unphysical pair correlation functions for small interparticle separation, whereas the pair correlation function obtained in the VS scheme is acceptable. Unfortunately, no such test has been made on the Geldart-Taylor $G(q)$.

Lacking a more exact theory, we do not know the precise form of $G(q)$ for intermediate values of q . In the limit of large q it has recently been shown¹¹ that

$$G(q) \rightarrow \frac{2}{3} [1 - g(0)] , \quad (48)$$

where $g(0)$ is the value of the pair correlation function at $r=0$. For values of $r_s \gtrsim 4$, one knows that $g(0)$ is nearly zero and, therefore, $G(\infty) \approx \frac{2}{3}$. One cannot rule out the possibility that the true $G(q)$ has a maximum for some intermediate value of q .

As an illustration we shall consider the exchange contribution to $K_{xc}(0)$. In this case

$$G(q) \xrightarrow{q \rightarrow 0} \left(1 + \frac{n}{2} \frac{\partial}{\partial n} \right) \frac{3}{8} \left(\frac{q}{q_F} \right)^2 = \frac{1}{4} \left(\frac{q}{q_F} \right)^2 \quad (49)$$

[see Eq. (22) of Ref. 1]. Here $a = \frac{1}{2}$ since $t(n) = t_0(n)$. From Eq. (47) we have

$$\begin{aligned} K_x(q) &= - (4\pi e^2 / q^2)^{1/4} (q / q_F)^2 \\ &= - \pi e^2 (3\pi^2 n)^{-2/3} . \end{aligned} \quad (50)$$

Hence, the exchange potential is

$$\begin{aligned} \mu_x(n) &= \int_0^n K_{xc}(n') dn' \\ &= - (e^2 / \pi) (3\pi^2 n)^{1/3} , \end{aligned} \quad (51)$$

which is the same as the Kohn-Sham exchange. This is, of course, expected since we have shown in Sec. III that the two procedures are identical in the long-wavelength limit.

V. GRADIENT CORRECTION TO EXCHANGE AND CORRELATION ENERGY

In this section we shall examine the lowest-order gradient correction to the combined exchange and correlation energy of a slightly inhomogeneous electron gas within the framework of the approximate scheme of VS. Hitherto, it has not been pos-

sible to calculate exactly even this lowest-order correction for all values of r_s of interest. Sham¹² was able to evaluate the exchange correction to order e^2 , and Ma and Brueckner¹³ evaluated the corresponding correlation correction valid for $r_s \ll 1$. The latter authors find that even in this limit the correlation correction is as large as 2.5 times the exchange correction. In the local density approximation, the total exchange and correlation energy is written as

$$\begin{aligned} E_{xc}[\langle n \rangle] &= \int d\vec{r} \epsilon_{xc}(n) \langle n(\vec{r}) \rangle \\ &+ \frac{1}{2} \int d\vec{r} g_{xc}^{(2)}(n) |\vec{\nabla} \langle n(\vec{r}) \rangle|^2 + \dots , \end{aligned} \quad (52)$$

where $\epsilon_{xc}(n)$ is the exchange and correlation energy per electron in the homogeneous electron gas with density n . The quantity $g_{xc}^{(2)}$ in Eq. (52), as shown by Kohn and Sham, is the coefficient of the q^2 term in the q expansion of $K_{xc}(q)$. According to Eq. (47) (47), $g_{xc}^{(2)}$ is, therefore, the q^2 coefficient in the expansion of $-v(q)G(q)$.

The essence of the VS scheme and of the earlier work⁷ is that it is self-consistent in the sense that the pair correlation function entering in $G(q)$ is the same as one obtains from the resulting response function. It is, therefore, not legitimate to separate exchange and correlation.

We do not have an analytic expression for the self-consistent $G(q)$ but for $q \lesssim 2k_F$, it can be well represented (to within $\frac{1}{2}\%$ accuracy) by the following expression¹:

$$G(q) = A \{ 1 - \exp[-B(q/k_F)^2] \} . \quad (53)$$

The parameters A and B are very gentle functions of r_s and have been tabulated by VS. $g_{xc}^{(2)}$, which is given by the coefficient of the q^2 term in the small- q expansion of $-v(q)G(q)$, is

$$g_{xc}^{(2)}(n) = \frac{2}{3} AB^2 \{ (e^2 / \pi) [n^{-4/3} / (3\pi^2)^{1/3}] \} . \quad (54)$$

Using the tabulated values of A and B , one finds that the factor $\frac{1}{3} 2AB^2$ in Eq. (54) changes from 0.064 for $r_s = 1$ to 0.055 for $r_s = 6$. For $r_s \ll 1$, it extrapolates to the value 0.066.

There is no exact calculation available for $g_{xc}^{(2)}$ for the range of metallic densities with which the above values can be compared. Such a comparison can, however, be made for $r_s \ll 1$. Ma and Brueckner¹³ find that the correlation correction in the local density approximation can be written as

$$\Delta E_c[\langle n \rangle] = \int d\vec{r} B_c(n) |\vec{\nabla} \langle n(\vec{r}) \rangle|^2 , \quad (55)$$

where

$$B_c(n) = \frac{1}{2} g_c^{(2)}(n) = 0.00847 n^{-4/3} \text{ Ry} . \quad (56)$$

To order e^2 , Sham's estimate for the corresponding exchange contribution is¹²

$$g_x^{(2)}(n) = -0.00667 n^{-4/3} \text{ Ry} . \quad (57)$$

The resultant exchange and correlation contribution is then

$$g_{xc}^{(2)}(n) = 0.01027 n^{-4/3} \text{ Ry} . \quad (58)$$

Our estimate for $r_s \ll 1$ is

$$g_{xc}^{(2)}(n) = 0.0136 n^{-4/3} \text{ Ry} . \quad (59)$$

We also have estimates through Eq. (54), of $g_{xc}^{(2)}$ in the metallic density range, and it would be interesting if one could check them through independent means.

VI. GRADIENT CORRECTION IN HARTREE-FOCK APPROXIMATION

We have preferred to discuss the Hartree-Fock approximation to the gradient correction in a separate section, for the reason that in some respects it is somewhat of a pathological case. Sham¹² has evaluated the coefficient $g_{xc}^{(2)}$ to order e^2 in Hartree-Fock approximation. It would, therefore, be of some interest to calculate the same quantity in the VS scheme, using the Hartree-Fock pair correlation function in the evaluation of $G(q)$ as was done in the illustrative example in Sec. IV. As was mentioned in Sec. V, this is really not legitimate, for by doing this we violate the basic requirement of self-consistency of the pair correlation function. We shall do this nonetheless.

Using Eq. (22) of Ref. 7, it is straightforward to show that

$$G_{\text{HF}}(q) = \left(1 + \frac{n}{2} \frac{\partial}{\partial n}\right) \left[\frac{3}{8} \left(\frac{q}{k_F}\right)^2 - \frac{31}{400} \left(\frac{q}{k_F}\right)^4 + \frac{6}{5} \left(\frac{q}{2k_F}\right)^4 \ln\left(\frac{q}{2k_F}\right) \right], \quad (60)$$

where we have ignored terms of order q^6 and higher. This then yields

$$-v(q) G_{\text{HF}}(q) \equiv K_x(q) = -\frac{\pi e^2}{(3\pi^2 n)^{2/3}} + \frac{23}{150} \frac{\pi e^2}{(3\pi^2 n)^{4/3}} q^2 - \frac{1}{10} \frac{\pi e^2}{(3\pi^2 n)^{4/3}} q^2 \ln \frac{q}{2k_F}. \quad (61)$$

We see that $g_x^{(2)}$ has a logarithmic singularity for $q \rightarrow 0$, implying that in this scheme no gradient expansion exists. In the exact calculation of Sham to order e^2 , only three graphs in the perturbation expansion contribute to $K_x(q)$. Each one of these graphs gives a singular contribution of the same kind as above, but they cancel out in the resultant contribution. This subtle cancellation is not present in the Hartree-Fock result of VS. Sham's result is

$$K_x(q) = -\frac{\pi e^2}{(3\pi^2 n)^{2/3}} - \frac{21}{216} \frac{\pi e^2}{(3\pi^2 n)^{4/3}} q^2, \quad (62)$$

which can be compared with Eq. (61). It is seen that in Eq. (61) we not only have an extra singular term but the sign of the q^2 term is wrong. It seems that the exact Hartree-Fock result, including all orders in e^2 , is not analytic for $q \rightarrow 0$.¹⁴ This would imply that the gradient expansion does not exist in the exact Hartree-Fock case.

The above discrepancy between the VS result and that of Sham indicates that violating the self-consistency requirement in the VS scheme should not be permitted. This is supported by the reasonable agreement for $g_{xc}^{(2)}$ obtained in Sec. V, where comparison with the result for $r_s \ll 1$ was made with both exchange and correlation included. The discrepancy above could also mean that in the VS scheme, exchange has not been treated as accurately as correlation. The reason for getting a fairly good agreement in Sec. V would then be that for $r_s \ll 1$, the correlation contribution to the gradient term dominates over the exchange contribution.

VII. REMARKS ON THE DIELECTRIC FUNCTION

The main question which now remains to be answered is how reliable the VS dielectric response function is for shorter wavelengths and finite frequencies. Let us recall that in the very first version of the theory,⁷ the principal aim was to take account of short-range correlations which reflect the behavior of fluctuations whose wavelengths are on the order of inverse Fermi wave vector. In this version one was able to remedy the bad behavior of the pair correlation function in the earlier theories. However, the compressibility obtained was unsatisfactory, which reflects the poor behavior of the theory for long wavelengths. This defect was remedied in the VS scheme by taking into account the adjustment of the nonequilibrium pair correlation function to the external potential [see Eq. (6)]. This modification gave a pair correlation function which, as regards its short-range behavior, was still acceptable. Sjölander and Stott¹⁵ have generalized the theory of Ref. 7 to the case of a two-component plasma and have successfully applied it to the calculation of the annihilation rates of positrons in metals. The latter depend chiefly on how well the short-range correlations are treated in the theory. We would conclude that in the VS scheme both the long- and short-range correlations are treated well.

Very recently, Yasuhara¹⁶ has investigated the short-range correlations in the electron gas at metallic densities from a diagrammatic analysis of the perturbation theory, and has concluded that it is essential to take into account an infinite sum of electron-electron ladder diagrams. An analo-

gous analysis has also been made by other authors.¹⁷⁻¹⁹ These authors have calculated the pair correlation function for various values of r_s and have compared their results with those of Singwi *et al.* and find a remarkably close agreement between the two. One is led to conclude that in the scheme of Singwi *et al.*⁷ the effective interaction is closely related to their t matrix.

So far we have been concerned only with the static aspects of the dielectric response. It was mentioned earlier that the phonon dispersion curves in simple metals are very well reproduced in the VS scheme. This still reflects only the static behavior of the theory. Recently one has been able to obtain experimental information^{20,21} on the dynamic form factor $S(\vec{q}, \omega)$ for the electron liquid in Be and in Al. Kalia and Mukhopadhyay²² have used the VS theory to calculate $S(\vec{q}, \omega)$ and have compared their calculation with the above mentioned experimental results. They find that both the calculated position and width of the broad peak in $S(\vec{q}, \omega)$ are in definite disagreement with the observations for $q > q_c$, q_c being the critical wave vector at which the plasmon dispersion curve joins the particle-hole continuum. The theory, therefore, in its present form is quite unsatisfactory for high-frequency phenomena and definitely needs improvement.

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APPENDIX

In the formalism of second quantization the Hamiltonian is

$$H(n) = -\frac{\hbar^2}{2m} \sum_{\sigma} \int d\vec{r} \psi_{\sigma}^{\dagger}(\vec{r}) \nabla^2 \psi_{\sigma}(\vec{r}) + \frac{1}{2} \sum_{\sigma\sigma'} \int d\vec{r} d\vec{r}' v(\vec{r} - \vec{r}') \times \psi_{\sigma}^{\dagger}(\vec{r}) \psi_{\sigma'}^{\dagger}(\vec{r}') \psi_{\sigma}(\vec{r}') \psi_{\sigma}(\vec{r}), \quad (\text{A1})$$

where the integrations extend over the volume V , containing N particles. We shall consider N as a fixed number, whereas V and thereby the density, $n = N/V$, is varied. From the variational principle it follows that

$$\frac{\partial}{\partial n} \langle 0 | H(n) | 0 \rangle = \langle 0 | \frac{\partial H(n)}{\partial n} | 0 \rangle, \quad (\text{A2})$$

where $|0\rangle$ is the ground state of $H(n)$ and depends on the density n . In order to make use of the above relation we need an expression for $H(n)$, where the density dependence appears explicitly. For this purpose we introduce a dimensionless position vector through

$$\vec{\xi} = V^{-1/3} \vec{r} \quad (\text{A3})$$

We introduce new field operators

$$\tilde{\psi}_{\sigma}(\vec{\xi}) = V^{-1/2} \psi_{\sigma}(\vec{r}), \quad (\text{A4})$$

so that they satisfy the usual commutation relation

$$\tilde{\psi}_{\sigma}(\vec{\xi}) \tilde{\psi}_{\sigma'}^{\dagger}(\vec{\xi}') + \tilde{\psi}_{\sigma'}^{\dagger}(\vec{\xi}') \tilde{\psi}_{\sigma}(\vec{\xi}) = \delta_{\sigma\sigma'} \delta(\vec{\xi} - \vec{\xi}'). \quad (\text{A5})$$

Performing the transformations defined by Eqs. (A3) and (A4), we obtain

$$H(n) = -\frac{(n/N)^{2/3}}{2m} \sum_{\sigma} \int d\vec{\xi} \tilde{\psi}_{\sigma}^{\dagger}(\vec{\xi}) \nabla_{\vec{\xi}}^2 \tilde{\psi}_{\sigma}(\vec{\xi}) + \frac{1}{2} \sum_{\sigma\sigma'} \int d\vec{\xi} d\vec{\xi}' v[(n/N)^{-1/3}(\vec{\xi} - \vec{\xi}')] \times \tilde{\psi}_{\sigma}^{\dagger}(\vec{\xi}) \tilde{\psi}_{\sigma'}^{\dagger}(\vec{\xi}') \tilde{\psi}_{\sigma}(\vec{\xi}') \tilde{\psi}_{\sigma}(\vec{\xi}). \quad (\text{A6})$$

It is now straightforward to differentiate $H(n)$ with respect to n , and then, going back to the original notation, we have

$$\frac{\partial}{\partial n} H(n) = \frac{2}{3n} \frac{\hbar^2}{2m} \sum_{\sigma} \int d\vec{r} \psi_{\sigma}^{\dagger}(\vec{r}) \nabla^2 \psi_{\sigma}^{\dagger}(r) - \frac{1}{6n} \sum_{\sigma\sigma'} \int d\vec{r} d\vec{r}' (\vec{r} - \vec{r}') \cdot \nabla v(\vec{r} - \vec{r}') \times \psi_{\sigma}^{\dagger}(r) \psi_{\sigma'}^{\dagger}(\vec{r}') \psi_{\sigma}(\vec{r}') \psi_{\sigma}(\vec{r}). \quad (\text{A7})$$

Using the definition of the pair correlation function

$$g(\vec{r} - \vec{r}'; n) = \frac{1}{n^2} \sum_{\sigma\sigma'} \langle 0 | \psi_{\sigma}^{\dagger}(\vec{r}) \psi_{\sigma'}^{\dagger}(\vec{r}') \psi_{\sigma}(\vec{r}') \psi_{\sigma}(\vec{r}) | 0 \rangle, \quad (\text{A8})$$

we obtain from (A2), (A1), and (A7)

$$\frac{5}{3} t(n) - n \frac{\partial t(n)}{\partial n} = \frac{1}{2} n^2 \int d\vec{r} v(r) \left(1 + n \frac{\partial}{\partial n} \right) g(r; n) + \frac{1}{6} n^2 \int d\vec{r} r \frac{dv(r)}{dr} g(r; n), \quad (\text{A9})$$

where $t(n)$ is the ground-state expectation value of the kinetic energy density. This equation differs from Eq. (14) of the text through the constant term

$$\frac{1}{2} n^2 \int v(r) d\vec{r} + \frac{1}{6} n^2 \int r \frac{dv(r)}{dr} d\vec{r},$$

which, however, vanishes because

$$\int \vec{r} \cdot \nabla v(r) d\vec{r} = -3 \int v(r) d\vec{r}. \quad (\text{A10})$$

For the electron gas one has to include the uniform positive background, which causes $g(r; n)$ in (A9) to be replaced by $g(r; n) - 1$, in which case (A9) is identical with Eq. (14).

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