

Self-consistent weighted-density approximation for the electron gas.

I. Bulk properties

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The weighted-density approximation provides a direct link between the electron-electron pair distribution function and the response function of a homogeneous electron gas. Here we propose to use this relation as a closure for the fluctuation-dissipation equations to obtain in a closed form all the bulk properties of the system. The results are compared with previous theories and computer simulations.

I. INTRODUCTION

In the density functional formalism (DFF) of Hohenberg, Kohn, and Sham,^{1,2} all ground-state properties of a paramagnetic electron gas, in the presence of an external potential $V_{\text{ext}}(\mathbf{r})$, can be expressed as functionals of the electron density $n(\mathbf{r})$. The total energy is usually written as

$$E[n(\mathbf{r})] = \int d\mathbf{r} V_{\text{ext}}(\mathbf{r})n(\mathbf{r}) + T_0[n(\mathbf{r})] + \frac{1}{2} \int \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + E_{\text{XC}}[n(\mathbf{r})], \quad (1.1)$$

where $T_0[n(\mathbf{r})]$ is, by definition, the kinetic energy of a system of noninteracting electrons. The third term in (1.1) is the Hartree energy due to the electron-electron interaction in a mean-field approximation, which neglects any electron-electron correlation. The last term, $E_{\text{XC}}[n(\mathbf{r})]$, is defined as the difference between the exact $E[n(\mathbf{r})]$ and the first three terms in Eq. (1.1). Atomic units $m_e = e = \hbar = 1$, are used throughout this work. The theorem proved by Hohenberg and Kohn¹ establishes that, for a given external potential, the ground-state density of electrons $n(\mathbf{r})$ minimizes $E[n(\mathbf{r})]$ and this minimum value is the ground-state energy E_0 . Thus one can reduce the many-body problem of N interacting electrons to a variational principle

$$\frac{\delta E[n(\mathbf{r})]}{\delta n(\mathbf{r})} = 0 \quad (1.2)$$

for the total density of particles. The problem in DFF is our ignorance of the explicit form of $E_{\text{XC}}[n]$ as a function of $n(\mathbf{r})$. The construction of approximations for E_{XC} is a topic of central importance in the application of DFF to inhomogeneous electron systems. A convenient starting point is provided by the exact expression³

$$E_{\text{XC}}[n(\mathbf{r})] = \frac{1}{2} \int d\mathbf{r} n(\mathbf{r}) \int d\mathbf{r}' \frac{n_{\text{XC}}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}, \quad (1.3)$$

where the exchange-correlation hole n_{XC} is defined as

$$n_{\text{XC}}(\mathbf{r}, \mathbf{r}') = n(\mathbf{r}') \int_0^1 [g_{n(\mathbf{r})}(\mathbf{r}, \mathbf{r}', \gamma) - 1] d\gamma \equiv n(\mathbf{r}') G(\mathbf{r}, \mathbf{r}') \quad (1.4)$$

and must obey the charge conservation rule

$$\int d\mathbf{r} n_{\text{XC}}(\mathbf{r}, \mathbf{r}') = -1. \quad (1.5)$$

In Eq. (1.4) $g_{n(\mathbf{r})}(\mathbf{r}, \mathbf{r}', \gamma)$ is the pair correlation function of a system with density $n(\mathbf{r})$ and pair interaction potential $\gamma/|\mathbf{r}-\mathbf{r}'|$. The density $n(\mathbf{r})$ is evaluated for the physical value $\gamma=1$. For homogeneous systems, $n(\mathbf{r})=n$, the function $g_{n(\mathbf{r})}(\mathbf{r}, \mathbf{r}', \gamma) = g(|\mathbf{r}-\mathbf{r}'|, n, \gamma)$ may be obtained from different theoretical approaches and computer simulations, but very little is known about it for inhomogeneous systems. It is then necessary to make some approximations in Eq. (1.3) before it can be used. The first attempt, and the most usual, is the so-called local-density approximation (LDA), which uses at each point the pair correlation function of a homogeneous electron liquid with density $n(\mathbf{r})$:

$$n_{\text{XC}}^{\text{LD}}(\mathbf{r}, \mathbf{r}') = n(\mathbf{r}) \int_0^1 d\gamma [g(|\mathbf{r}-\mathbf{r}'|, n(\mathbf{r}), \gamma) - 1]. \quad (1.6)$$

This exchange-correlation hole verifies (1.5) because the sum rule is satisfied by the homogeneous system $g(r, n, \gamma)$. Usually the LDA is written as

$$E_{\text{XC}}[n(\mathbf{r})] = \int d\mathbf{r} n(\mathbf{r}) \epsilon_{\text{XC}}(n(\mathbf{r})), \quad (1.7)$$

where

$$\epsilon_{\text{XC}}(n(\mathbf{r})) = \frac{1}{2} \int d\mathbf{r}' \frac{n_{\text{XC}}^{\text{LD}}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \quad (1.8)$$

is the exchange-correlation (XC) energy per electron in a homogeneous system of density $n(\mathbf{r})$. In fact, the LDA does not need explicit knowledge of the pair distribution function. $\epsilon_{\text{XC}}(n)$ is the only information required and in practice it is obtained without reference to Eqs. (1.3)–(1.6). This crude approximation has been applied to many systems and the results have been more accurate than there was any reason to expect. In the last

years several nonlocal approximations to the XC energy functional have been developed in attempts to find a justification for the LDA and to improve it. The first attempt was based on the expansion of $E_{XC}[n(\mathbf{r})]$ in powers of the gradient of $n(\mathbf{r})$ up to second order.⁴⁻⁷ Later on, Langreth and Perdew^{8,9} developed the nonlocal wave-vector analysis which involves a decomposition of the surface XC energy σ_{XC} in contributions $\sigma_{XC}(k)$ from density fluctuations of wave vector k . Langreth and Mehl¹⁰ have constructed a modified gradient expansion based on the wave-vector analysis.

Gunnarsson *et al.*³ have developed two nonlocal schemes based on Eq. (1.3), where n_{XC} depends on some average of the surrounding electron density, instead of the local density as in the LDA. The average density approximation (ADA) replaces the prefactor $n(\mathbf{r}')$ in (1.4) by an averaged density $\bar{n}(\mathbf{r})$ at which the pair correlation function is also evaluated:

$$n_{XC}^{ADA}(\mathbf{r}, \mathbf{r}') = \bar{n}(\mathbf{r}) \int_0^1 d\gamma [g(|\mathbf{r} - \mathbf{r}'|, \bar{n}(\mathbf{r}), \gamma) - 1] \quad (1.9)$$

with

$$\bar{n}(\mathbf{r}) = \int d\mathbf{r}' w(|\mathbf{r} - \mathbf{r}'|; \bar{n}(\mathbf{r}')) n(\mathbf{r}'), \quad (1.10)$$

where $w(r, n)$ is a weight function to be determined. In the ADA the XC energy functional becomes

$$E_{XC}[n(\mathbf{r})] = \int n(\mathbf{r}) \epsilon_{XC}(\bar{n}(\mathbf{r})) d\mathbf{r}. \quad (1.11)$$

The ADA also satisfies the charge conservation rule (1.5) by construction, and it does not require knowledge of $g(r, n, \gamma)$, since $\epsilon_{XC}(n)$ may be obtained independently of Eq. (1.9). The weight function, $w(r, n)$, is chosen to recover the limit of the weakly inhomogeneous electron liquid or, which is equivalent, the response function of the system given by the second functional derivative of the total energy $E[n(\mathbf{r})]$:¹

$$\begin{aligned} -\chi^{-1}(\mathbf{r}, \mathbf{r}') &= \frac{\delta E[n]}{\delta n(\mathbf{r}) \delta n(\mathbf{r}')} \\ &= K_0(\mathbf{r}, \mathbf{r}') + \frac{1}{|\mathbf{r} - \mathbf{r}'|} + U_{XC}(\mathbf{r}, \mathbf{r}'), \end{aligned} \quad (1.12)$$

where K_0 and U_{XC} are, respectively, the second functional derivatives of $T_0[n(\mathbf{r})]$ and $E_{XC}[n(\mathbf{r})]$. In a homogeneous system the Fourier transform of $U_{XC}(|\mathbf{r} - \mathbf{r}'|)$ is

$$U_{XC}(q, n) = -\frac{4\pi}{q^2} G_{XC}(q, n), \quad (1.13)$$

where $G_{XC}(q, n)$ is the so-called static local-field correction to the dielectric function and describes the contribution of $E_{XC}[n(\mathbf{r})]$ to the response function of the system. To use the ADA we need to know $\epsilon_{XC}(n)$ and $G_{XC}(q, n)$ for a homogeneous system. Unfortunately there are large discrepancies between the several ap-

proaches used to evaluate $G_{XC}(q, n)$. This leads to an uncertainty in the evaluation of surface properties within this scheme.¹¹

The second theory of Gunnarsson *et al.*³ is the weighted-density approximation (WDA) which also replaces the pair correlation function in (1.4) for that of a homogeneous electron gas, the main difference with the ADA being that it keeps the proper density prefactor in (1.4):

$$n_{XC}^{WD}(\mathbf{r}, \mathbf{r}') = n(\mathbf{r}') \int_0^1 d\gamma [g(|\mathbf{r} - \mathbf{r}'|, \bar{n}(\mathbf{r}), \gamma) - 1]. \quad (1.14)$$

This implies a new procedure to determine the average density $\bar{n}(\mathbf{r})$ so that (1.14) verifies the sum rule (1.5). Thus the only input required by the WDA is the pair distribution function of the homogeneous electron gas, integrated over the coupling parameter and as a function of the density. The first calculation with the WDA (Ref. 3) used the random-phase approximation (RPA) $g(r, n, \gamma)$. Afterwards, a simple parametrized expression was introduced by Gunnarsson and Jones,¹² in an attempt to reproduce the image potential outside a metal surface. Unfortunately, this very simple empirical form has been extensively used by other authors,^{13,14} without a thoughtful study of the effects of this choice on the evaluated properties. We have found that the results for the surface energy are strongly biased by the choice of $g(r, n, \gamma)$ and, moreover, the position of the image plane given by the WDA with this prescription is unphysical.

On the other hand, from the input of the pair distribution function, the WDA gives a prescription for the XC energy and the response function of the system. Thus contrary to other density-functional models, like LDA and ADA, it provides a nontrivial link between bulk properties like the structure factor, $S(q, n)$, and $G_{XC}(q, n)$. What we propose here is to use this WDA relationship, together with the fluctuation-dissipation theorem, to obtain a self-consistent evaluation of all the bulk properties of the electron liquid. The result, which we call the "self-consistent weighted-density approximation" (SC-WDA), is the first density functional model for $E_{XC}[n(\mathbf{r})]$ which does not require any external input from independent theories for the bulk properties. The work is presented in two articles. This first one develops the self-consistency scheme to obtain the bulk properties of the electron liquid within the SC-WDA. These are compared with the existent results for $\epsilon_{XC}(n)$, $g(r, n, \gamma)$, and $G_{XC}(q, n)$, from both other theories and computer simulations. In the second paper of the series we apply the SC-WDA to the study of metal surfaces, within the jellium model, and compare them with the previous results.

II. THEORY: SC-WDA

The second functional derivative of $E_{XC}[n(\mathbf{r})]$ evaluated at a homogeneous system with density $n(\mathbf{r}) = n$ is easily obtained from (1.3) and (1.14):

$$\begin{aligned}
\frac{\delta E_{\text{XC}}[n]}{\delta n(\mathbf{r})\delta n(\mathbf{r}')}\bigg|_{n(\mathbf{r})=n} &= \frac{G(|\mathbf{r}-\mathbf{r}'|,n)}{|\mathbf{r}-\mathbf{r}'|} - n^2 G(|\mathbf{r}-\mathbf{r}'|,n) \frac{d}{dn} \left[\int d\mathbf{r}_1 \frac{G(r_1,n)}{r_1} \right] \\
&\quad - n^2 \int d\mathbf{r}_1 \frac{d}{dn} \left[\frac{G(|\mathbf{r}-\mathbf{r}_1|,n)}{|\mathbf{r}-\mathbf{r}_1|} \right] G(|\mathbf{r}'-\mathbf{r}_1|,n) \\
&\quad + \frac{1}{2} n^4 \frac{d^2}{dn^2} \left[\int d\mathbf{r}_2 \frac{G(r_2,n)}{r_2} \right] \int d\mathbf{r}_1 G(|\mathbf{r}-\mathbf{r}_1|,n) G(|\mathbf{r}_1-\mathbf{r}'|,n) \\
&\quad + \frac{1}{2} n^2 \frac{d}{dn} \left[\int d\mathbf{r}_2 \frac{G(r_2,n)}{r_2} \right] \frac{d}{dn} \left[n^2 \int d\mathbf{r}_1 G(|\mathbf{r}-\mathbf{r}_1|,n) G(|\mathbf{r}_1-\mathbf{r}'|,n) \right], \quad (2.1)
\end{aligned}$$

where $G(r,n)$ is defined from (1.4) for bulk systems. By taking the Fourier transform of (2.1) we get

$$\begin{aligned}
U_{\text{XC}}(q,n) &= F(q,n) - 2n \frac{d}{dn} \left[\frac{\epsilon_{\text{XC}}(n)}{n} \right] nG(q,n) - n \frac{dF(q,n)}{dn} nG(q,n) + n^2 \frac{d^2}{dn^2} \left[\frac{\epsilon_{\text{XC}}(n)}{n} \right] [nG(q,n)]^2 \\
&\quad + 2n \frac{d}{dn} \left[\frac{\epsilon_{\text{XC}}(n)}{n} \right] nG(q,n) n \frac{d}{dn} [nG(q,n)], \quad (2.2)
\end{aligned}$$

where

$$G(q,n) = \int d\mathbf{r} e^{iq\cdot\mathbf{r}} G(r,n)$$

and

$$F(q,n) = \int d\mathbf{r} e^{iq\cdot\mathbf{r}} \frac{G(r,n)}{r}.$$

Equation (2.2) relates the static local-field correction $G_{\text{XC}}(q,n)$ to $G(q,n)$ which is the integral over the coupling constant of the static structure factor $S(q,n,\gamma)$:

$$G(q,n) = \int_0^1 d\gamma [S(q,n,\gamma) - 1]. \quad (2.3)$$

Following Singwi *et al.*,¹⁵ a combination of this equation with the fluctuation-dissipation theorem leads to a self-consistent formulation which may be solved numerically by an iterative method. This procedure starts in the generalized RPA expression for the dielectric function and approximates the XC contribution by the static $G_{\text{XC}}(q,n)$:

$$\frac{1}{\epsilon(q,\omega)} = \frac{1 + v(q)G_{\text{XC}}(q,n)\chi_0(q,\omega)}{1 - v(q)[1 - G_{\text{XC}}(q,n)]\chi_0(q,\omega)}, \quad (2.4)$$

where $\chi_0(q,\omega)$ is the Lindhard polarizability and $v(q) = 4\pi/q^2$ is the Fourier-transformed Coulomb potential.

According to the fluctuation-dissipation theorem, $S(q,n)$ can be calculated from $\epsilon(q,\omega)$ as

$$S(q,n) = -\frac{1}{\pi n v(q)} \int_0^\infty d\omega \text{Im} \left[\frac{1}{\epsilon(q,\omega)} \right]. \quad (2.5)$$

Thus, the three equations (2.4), (2.5), and (2.2) link the three functions $S(q,n)G_{\text{XC}}(q,n)$, $S(q,n)$, and $\epsilon(q,\omega)$, and can be solved self-consistently on the computer. The main difficulty in order to close the procedure is the integration over the coupling constant γ in Eq. (2.3). Here we will simplify the calculation by means of a scaling approximation. We start by defining the function

$G(r,n,\gamma)$ to describe the correlation in a system with density n and coupling parameter γ :

$$G(r,n,\gamma) = \frac{1}{\gamma} \int_0^\gamma d\xi (g(r,n,\xi) - 1), \quad (2.6)$$

and we assume that this function has the scaled form

$$G(r,n,\gamma) = C(r_s,\gamma) \hat{G} \left[\frac{r 2k_F(n)}{\lambda(r_s,\gamma)} \right] \quad (2.7)$$

with the usual definition of the Fermi wave vector k_F . Thus the single variable function $\hat{G}(y)$ gives the shape of $G(r,n,\gamma)$ and the functions $C(r_s,\gamma)$ and $\lambda(r_s,\gamma)$ define the scales as functions of the density [$n = 3/(4\pi r_s^3)$] and the coupling γ . This kind of scaled form of $G(r,n,\gamma)$ has been previously used in WDA and it seems to be in fair agreement with the existing results for $g(r,n,\gamma)$ (at $\gamma=1$) in the metallic range of r_s .¹⁶ The dependence of the functions $C(r_s,\gamma)$ and $\lambda(r_s,\gamma)$ may be simplified by the use of the normalization condition (1.5) and the evaluation of the XC energy per particle in a homogeneous system from (1.3) at each value of n and γ . That gives

$$nC(r_s,\gamma) \frac{\lambda(r_s,\gamma)^3}{[2k_F(r_s)]^3} = A_2, \quad (2.8)$$

and

$$\epsilon_{\text{XC}}(r_s,\gamma) = \gamma \frac{n}{2} C(r_s,\gamma) \frac{\lambda(r_s,\gamma)^2}{4k_F(r_s)^2} \frac{1}{A_1}, \quad (2.9)$$

where

$$1/A_1 = \int dy \frac{\hat{G}(y)}{y}$$

and

$$-1/A_2 = \int dy \hat{G}(y).$$

It is known¹⁷ that the XC energy of a system with

coupling constant γ is exactly γ^2 times the XC energy of a system with the full Coulomb interaction ($\gamma=1$), but a different density ($r'_s=\gamma r_s$):

$$\epsilon_{\text{XC}}(r_s, \gamma) = \gamma^2 \epsilon_{\text{XC}}(\gamma r_s, \gamma=1). \quad (2.10)$$

This may be compared with (2.9) to obtain

$$\lambda(r_s, \gamma) = \left[\frac{9\pi}{4} \right]^{1/3} \frac{A_2}{A_1} \frac{1}{r_s \epsilon_{\text{XC}}(\gamma r_s, \gamma=1)} = \lambda(\gamma r_s), \quad (2.11)$$

where from here onwards we omit the dependence on γ for $\gamma=1$.

It is now easy to obtain a relation between $G(r, n, \gamma)$ and $g(r, n, \gamma)$. For this, we differentiate (2.6) with respect to γ

$$\begin{aligned} g(r, n) - 1 &= \frac{d}{d\gamma} (\gamma G(r, n, \gamma)) \Big|_{\gamma=1} \\ &= G(r, n) + \frac{dC(\gamma r_s)}{d\gamma} \Big|_{\gamma=1} \hat{G}(y) \\ &\quad - C(r_s) \frac{d\hat{G}}{dy} \frac{y}{\lambda(r_s)} \frac{d\lambda(\gamma r_s)}{d\gamma} \Big|_{\gamma=1}, \end{aligned} \quad (2.12)$$

where $y = r2k_F/\lambda(r_s)$. Making use of the relations (2.12) and (2.11) we obtain

$$g(r, n) - 1 = G(r, n) [1 - 3R(r_s)] - R(r_s) C(r_s) y \frac{d\hat{G}(y)}{d(y)}, \quad (2.13)$$

where

$$R(r_s) = \frac{r_s}{\lambda(r_s)} \frac{d\lambda(r_s)}{dr_s}.$$

The Fourier transform of (2.13) is equal to

$$S(q, n) - 1 = 24\pi^2 A_2 \left[\hat{G}(\eta) + R(r_s) \eta \frac{d\hat{G}(\eta)}{d\eta} \right], \quad (2.14)$$

where

$$\hat{G}(\eta) = \int dy \hat{G}(y) e^{i\eta y}$$

and

$$\eta = \frac{q\lambda(r_s)}{2k_F(r_s)}.$$

Equation (2.13) gives the relation, within the scaled theory, between the integrated exchange and correlation hole $G(r, n)$ and the real exchange and correlation hole at each density and coupling constant $\gamma=1$. With this relation we may close the self-consistent procedure. Equation (2.2) is now written in a very simple form

$$\begin{aligned} U_{\text{XC}}(q, n) &= 2p A_1 \hat{F}(\eta) - 2p' A_2 \hat{G}(\eta) - 2A_1 A_2 \left[p' \hat{F}(\eta) - p \left(1 + \frac{p'}{p} \right) \eta \hat{F}'(\eta) \right] \hat{G}(\eta) \\ &\quad + A_2^2 p'' \hat{G}(\eta)^2 - 2A_2^2 p' \left[1 + \frac{p'}{p} \right] \hat{G}(\eta) \eta \hat{G}'(\eta), \end{aligned} \quad (2.15)$$

where

$$p = \frac{\epsilon_{\text{XC}}(n)}{n}, \quad p' = n \frac{dp}{dn}, \quad p'' = n^2 \frac{d^2 p}{dn^2},$$

and

$$\hat{F}(\eta) = \int dy \hat{G}(y) / y e^{i\eta y}.$$

The set of equations (2.4), (2.5), (2.14), and (2.15) may be solved numerically by an iterative method and will produce all physical magnitudes for a homogeneous electron gas. Before making the self-consistent determination it is necessary to point out that the scaling hypothesis (2.7) gives some problems. The first is in the limit $q \rightarrow \infty$ of $[q^4(1-S(q, n))]$, which from Eq. (2.13) is written as

$$\begin{aligned} \lim_{q \rightarrow \infty} q^4(1-S(q, n)) \\ = \frac{8k_F^3}{3\pi} C(r_s) \hat{G}'(y=0) \frac{2k_F}{\lambda(r_s)} [1 - 4R(r_s)], \end{aligned} \quad (2.16)$$

while Eq. (2.19) gives

$$\begin{aligned} \lim_{q \rightarrow \infty} U_{\text{XC}}(q, n) &= \lim_{q \rightarrow \infty} 2p A_1 \hat{F}(\eta) \\ &= \lim_{q \rightarrow \infty} v(q) C(r_s) \hat{G}(y=0). \end{aligned}$$

Substituting this value in (2.4) and integrating with respect to ω (2.5), we obtain a different limit for the structure factor form $S(q, n)$,

$$\lim_{q \rightarrow \infty} q^4(1-S(q, n)) = \frac{8k_F^3}{3\pi} [1 - C(r_s) \hat{G}(y=0)]. \quad (2.17)$$

Both Eqs. (2.17) and (2.18) can be equal only if the condition

$$\frac{2k_F}{\lambda(r_s)} [1 - 4R(r_s)] = \frac{[1 - G(y=0)]}{\hat{G}'(y=0)} = \text{const} \quad (2.18)$$

is satisfied. The second problem comes for $q \rightarrow 0$. It is known that in this limit the static structure factor is fully determined by the plasmon frequency ω_p :

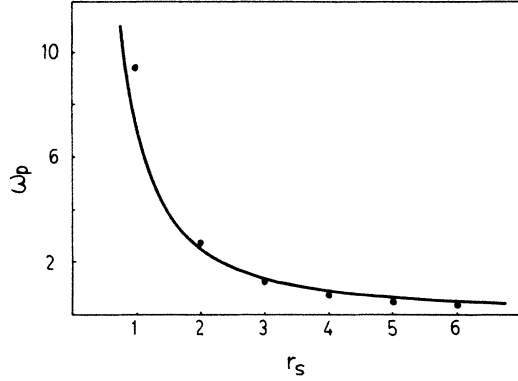


FIG. 1. Comparison between the exact frequency of the plasmon (2.19) (solid line) and that obtained using (2.20) (solid circles). The units are 10^{16} Hz.

$$\lim_{q \rightarrow 0} S(q, n) = \frac{q^2}{2\omega_p} \propto r_s^{3/2}. \quad (2.19)$$

In our theory it is very easy to show, from (2.14), that this limit is equal to

$$\lim_{q \rightarrow 0} S(q, n) = 12\pi^2 A_2 \hat{G}''(\eta=0) \left[\frac{\lambda(r_s)}{2k_F} \right]^2 [1 + 2R(r_s)] q^2, \quad (2.20)$$

so that both equations will have the same dependence with respect to r_s only if

$$r_s^{3/2} \left[\frac{\lambda(r_s)}{2k_F} \right]^2 [1 + 2R(r_s)] = \text{const}. \quad (2.21)$$

Equations (2.18) and (2.21) impose constraints on $\epsilon_{XC}(r_s)$, through $R(r_s)$ and $\lambda(r_s)$, so that each one could in principle be satisfied separately, but not both of them together. In fact, realistic descriptions of ϵ_{XC} do not satisfy either of them. This indicates that our present results are not fully consistent. However, despite the different dependence of the plasmon frequency on r_s given by (2.20), the numerical values obtained in the metallic density range are close enough to the exact results (see Fig. 1), so that the inconsistency associated to the scaling approximation (2.7) is not very important in practice.

III. NUMERICAL RESULTS

In this section we present the results of the self-consistent evaluation of the pair correlation function $g(r, n)$, the correlation energies, and $G_{XC}(q, n)$ in the metallic density range. We have solved the integro-differential equation (2.15) in an approximative way by

means of parametrized trial functions for $\hat{G}(y)$:

$$\hat{G}(y) = e^{-y^2} \sum_{i=0}^3 c_i y^i + e^{-\alpha y} \sum_{i=0}^2 d_i y^i \quad (3.1)$$

[$c_0 = 1$ is fixed so as not to be redundant with the scaling form (2.7)] and the XC energy

$$\epsilon_{XC}(r_s) = \epsilon_x(r_s) + \epsilon_c(r_s) = -\frac{0.916 \text{ Ry}}{r_s} + \frac{e_1}{1 + e_2 r_s^{1/2} + e_3 r_s}, \quad (3.2)$$

which is used to determine λ in (2.11). The form (3.1) is taken to have exponential decay as $y \rightarrow \infty$, and to be analytical everywhere, so that the structure factor $S(q, n)$ has a well-behaved limit at $q \rightarrow 0$ which is essential to reproduce the plasmon behavior. [Notice that this is not achieved with the empirical $G(r, n)$ fixed to obtain the image potential.¹³] We start the iteration scheme with the parameters fixed by the best fit to the Hartree-Fock structure factor, $S_{HF}(q, n)$, with limited accuracy because of the qualitative differences between $S_{HF}(q, n)$ and our parametrized form. From the fit to $S(q, n)$ we obtain the analytical expression for $G_{XC}(q, n)$ given by the WDA (2.15) and this is used in the numerical integration over ω (2.5) to obtain the new structure factor. A new set of parameters is now fixed to fit the new $S(q, n)$, taking special care of the decay at large q . The new parameters are used to obtain again $G_{XC}(q)$ and the procedure is repeated until convergence is achieved and the relative change of the parameters is less than 0.001. The parametrized forms (3.1) and (3.2) provide a fairly good agreement between the final $S(q)$ coming from the numerical integration on ω and its best fit. We must point out here the importance of a careful fit at each step of the iteration which may sometimes be difficult to achieve due to the large number of parameters used. As we have said before, our scaling hypothesis (2.7) is not fully consistent with the result of the integration (2.5), so that the set of parameters resulting from the iteration scheme would depend slightly on the value of r_s at which it is performed. We have done a global fit to several values of r_s within the metallic density range, from $r_s = 1$ to 6. In Table I we give the values obtained for the parameters.

In Fig. 2 we show the results obtained for the correlation energy compared with the Monte Carlo simulation of Ceperley and Alder,¹⁸ the variational Fermi hypernetted chain (FHN) theory of Lantto,¹⁶ and also with the results of Singwi *et al.*^{15,19} Our results are very close to the Ceperley-Alder simulation data¹⁸ and are indistinguishable from the original result of Singwi *et al.*,¹⁵ with a theory which does not verify the compressibility sum rule. The modification by Vashista and Singwi¹⁹ to approximate this sum rule leads to a slightly worse $\epsilon_c C(r_s)$ which is also shown in Fig. 2.

TABLE I. Values of the parameters used in Eqs. (3.1) and (3.2) for the best fit of $\hat{G}(y)$ and $\epsilon_c C(r_s)$. The parameter e_1 is given in Ry and the others are dimensionless.

c_1	c_2	c_3	α	d_0	d_1	d_2	e_1	e_2	e_3
-0.610 40	0.323 23	-0.349 36	3.442 90	0.256 90	0.121 33	5.1368	-0.477 01	2.313 20	0.471 90

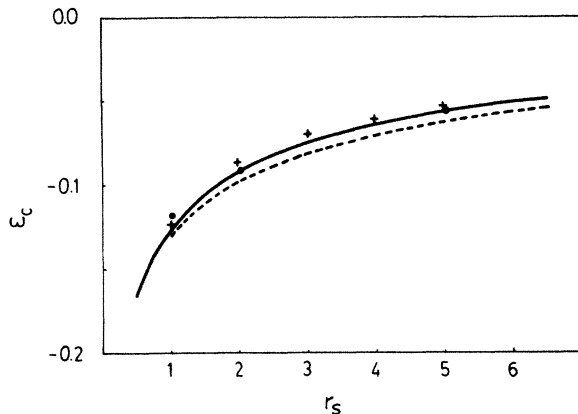


FIG. 2. Correlation energy $\epsilon_c(r_s)$ (Ry) vs r_s . The solid curve represents the values obtained in the present theory. The dashed curve refers to Vashista and Singwi (Ref. 19). The solid circles are the simulation results of Ceperley and Alder (Ref. 18), and the crosses the variational calculation of Lantto (Ref. 16).

In Fig. 3 we compare the radial distribution function we obtain with the results of Lantto,¹⁶ for $r_s=3$ and 5. The SC-WDA gives very good global agreement in all the metallic range and only for large r_s (greater than 5) $g(r=0, n)$ may become slightly negative as a remanent of the problems with the scaled form (2.7). Nevertheless, the results obtained in the proposed self-consistent procedure are as good as any previous theory.

In Fig. 4 we compare the function $G_{XC}(q)/q^2$ for $r_s=4$ obtained with different theories. There are two significant points in our result: the curvature at $q=0$ is small but positive and it has a rather sharp drop around $q=2k_F$. Both results are in agreement with that obtained by Geldart-Taylor²⁰ with a diagrammatic perturbation theory, and by Toigo and Woodruff²¹ with a theory based on the equation of motion for Green's func-

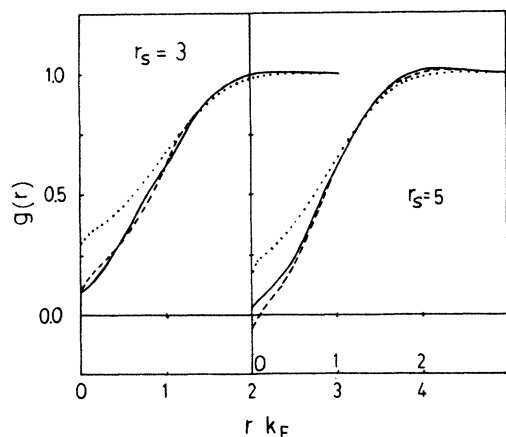


FIG. 3. Pair-correlation function $g(r, n)$ vs $k_F r$ for $r_s=3$ and 5. Dashed curve, present theory; solid curve, variational calculation of Lantto (Ref. 16). The dotted curve represents the function $G(r, n) + 1$, i.e., the pair-correlation function integrated over the coupling constant.

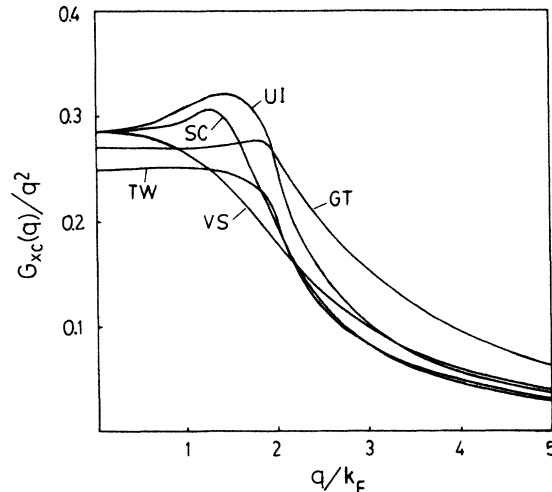


FIG. 4. The function $G_{XC}(q)/q^2$ vs q/k_F for $r_s=4$, for the present theory (SC), and the results of Geldart and Taylor (GT) (Ref. 20), Vashista and Singwi (VS) (Ref. 19), Utsumi and Ichimaru (UI) (Ref. 22), and Toigo and Woodruff (TW) (Ref. 21).

tions and involving decoupling approximations guided by the conservation of the momentum. Our result is in contrast with that obtained by Singwi *et al.*¹⁵ using a self-consistent procedure similar to ours. A clear advantage of the SC-WDA as a theory for bulk properties is that it satisfies by construction the compressibility sum rule, which is not achieved by Singwi *et al.*¹⁵ and only approximately by Vashista and Singwi.¹⁹ Utsumi and Ichimaru have also developed a self-consistent theory,²² but they split $G_{XC}(q, n)$ into an exchange part $G_x(q, n)$, which is fixed to satisfy several limits, and the remainder $G_c(q, n)$ for which the self-consistency is done. Our experience is that the self-consistency procedure is quite "soft" in the sense that the initial functions used may partially control some aspects of the final results. In the case of Utsumi and Ichimaru the final $G_{XC}(q, n)$ seem to be very close to the function $G_x(q, n)$ fixed *ad hoc*, while the SC-WDA does not require any external input at all.

IV. CONCLUSIONS

The WDA originally proposed by Gunnarsson *et al.*³ as a density functional model for the exchange and correlation energy of inhomogeneous electron systems, provides a direct link between electron-electron correlation function, the XC energy per electron, and the response function of a homogeneous system. Here we propose to use these relationships as a closure for the fluctuation-dissipation equations which connect the structure factor, $S(q, n)$, and the static local field correction to the RPA, $G_{XC}(q, n)$, so that all the bulk properties of the electron liquid may be obtained in a self-consistent way without any external input. This is equivalent to the method of Singwi *et al.*¹⁵ but the closure they used, based on the equation of motion for the screening charge, is substituted by the density functional relation

given by the WDA. The main approximation done by the WDA is the use of a correlation hole with spherical symmetry even if the system has nonhomogeneous density distribution. This may be a serious misrepresentation for strongly inhomogeneous systems, but it seems to be a quite sensible approximation in the evaluation of the response function from a homogeneous bulk. The main difficulty in the use of this scheme is the need to perform the integration of the structure factor with respect to the coupling parameters, which depends on the Coulomb interactions. In this paper we have simplified the problem by means of the scaling relation (2.7), which is not exact but seems to provide a good starting point.

The results obtained with the SC-WDA implemented with the scaling relation are quite satisfactory. The correlation energy per electron, as a function of the density, is very close to the results of computer simulations and comparable with the best theories at the present. Moreover, the compressibility sum rule which relates the derivatives of $\epsilon_{XC}(n)$ to the $q \rightarrow 0$ limit of $G_{XC}(q)/q^2$, is exactly satisfied in our theory, which is not the case for the results of Singwi *et al.*¹⁵ The shape of the XC hole given by the SC-WDA is also in very good agreement with the FHN results of Lantto.¹⁶

It is more difficult to analyze the results for the XC contribution to the response function, $U_{XC}(q)$, because there are no simulation results for this function, and earlier theories are spread over a wide range. However, it

is worthwhile to point out that, contrary to some previous self-consistent calculations,¹⁵⁻¹⁹ our $U_{XC}(q)$ has positive curvature at $q=0$ and a sharp decay around $q = 2k_F$.

The calculations presented here have been done in an approximate variational way, with a parametrized trial function for the XC hole. We believe that the accuracy obtained with this method is good enough and it has the practical advantage of making our results very easy to use. In this respect the theory presented here is the first self-consistent evaluation for the properties of the bulk electron liquid, with a natural extension to the study of inhomogeneous systems, for which the use of a parametrized $g(r,n)$ may be of practical interest. Work is in progress now to solve the SC-WDA equations without the scaling relation (2.8). This will remove the inconsistency (2.17)–(2.21), which nevertheless does not seem to be very important for the evaluation of the more relevant properties.

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