Uniform electron gas from the Colle-Salvetti functional: Missing long-range correlations

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Colle and Salvetti [Theor. Chim. Acta **37**, 329 (1975)] approximated the correlation energy of a many-electron system as a functional of the Hartree-Fock one-particle density matrix. The most fundamental and least approximate version of this functional [their Eq. (9)] is found to yield only 25% of the true correlation energy of a uniform electron gas, and not 100% as previously believed. While short-range correlations are described surprisingly well by this approach, important long-range correlations are missing. Such correlations are energetically negligible in atoms, but cannot be ignored in more extended systems, including solids as well as molecules.

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I. INTRODUCTION

The correlation energy is the correction to the Hartree-Fock energy of a many-electron system. Starting from a pair-correlated many-electron wave function, Colle and Salvetti [1,2] approximated the correlation energy as a functional of the one-particle Hartree-Fock density matrix $\rho_1^{\mathrm{HF}}(\mathbf{r},\mathbf{r}')$. Later Lee, Yang, and Parr [3] transcribed the Colle-Salvetti (CS) approximation into a widely used gradient-corrected functional of the electron density $n(\mathbf{r})$. The CS work also provided a motivation for more recent density functionals that employ the orbital kinetic energy density [4].

An early study by McWeeny [5] found that the most fundamental and least approximate form of the CS approach, Eq. (9) of Ref. [1], gave an accurate correlation energy per electron for the electron gas of uniform density, supporting the underlying CS approach. Encouraged by this result, Rajagopal, Kimball, and Banerjee (RKB) [6] made a CS-like ansatz for the pair-distribution function of a magnetic electron gas; long-range correlations were later built into the RKB model by Contini, Mazzone, and Sacchetti [7].

In the present work, however, we have not been able to reproduce the original result of Ref. [5]. We find instead that Eq. (9) of Ref. [1] underestimates the magnitude of the correlation energy by about a factor of 4. Our result is consonant with a recent critique by Singh, Massa, and Sahni [8] of the CS wave function for the two-electron atom, which in particular points out that it is not normalized.

It is widely known that the CS correlation energy functional is accurate for smaller atoms [9,10], but not for molecules where it misses important long-range correlations [2,11,12] which must be described by other approaches such as the configuration interaction method. We show here that the electron gas also has energetically important long-range correlations which are missed by all variants of the CS correlation energy functional. In both the electron gas [13,14] and molecules [15–17], the exact correlation hole has a long-range part which is approximately cancelled by the long-range part of the exact exchange hole, an effect which could have been but was not included in the CS approach.

II. ELECTRON PAIR DENSITIES, ETC.

We begin with a review of definitions [18]. Given an N-electron wave function $\Psi(\mathbf{r}_1\sigma_1,\ldots,\mathbf{r}_N\sigma_N)$, we define the pair density

$$\rho_2(\mathbf{r},\mathbf{r}')=N(N-1)\times\sum_{\sigma_i=1}^{N}\int\prod_{j=3}^{N}d\mathbf{r}_j|\Psi(\mathbf{r}\sigma_1,\mathbf{r}'\sigma_2,\ldots\mathbf{r}_N\sigma_N)|^2, \quad (1)$$

the one-particle density matrix

$$\rho_1(\mathbf{r},\mathbf{r}')=N\sum_{\sigma_i=1}^{N}\int\Psi^*(\mathbf{r}\sigma_1,\mathbf{r}_2\sigma_2,\ldots,\mathbf{r}_N\sigma_N)\times\Psi(\mathbf{r}'\sigma_1,\mathbf{r}_2\sigma_2,\ldots\mathbf{r}_N\sigma_N)d\mathbf{r}_2\ldots d\mathbf{r}_N, \quad (2)$$

and the electron density

$$n(\mathbf{r})=\rho_1(\mathbf{r},\mathbf{r})=\frac{1}{N-1}\int d\mathbf{r}'\,\rho_2(\mathbf{r},\mathbf{r}'). \quad (3)$$

While $n(\mathbf{r})d\mathbf{r}$ is the probability of finding an electron in $d\mathbf{r}$, $\rho_2(\mathbf{r},\mathbf{r}')d\mathbf{r}\,d\mathbf{r}'$ is the probability of finding one electron in $d\mathbf{r}$ and another in $d\mathbf{r}'$. We also define the pair-distribution function $g(\mathbf{r},\mathbf{r}')$:

$$\rho_2(\mathbf{r},\mathbf{r}')=n(\mathbf{r})n(\mathbf{r}')g(\mathbf{r},\mathbf{r}'). \quad (4)$$

By integrating Eq. (1) over $\mathbf{r}'$, we find that

$$\int d\mathbf{r}'\,n(\mathbf{r}')[g(\mathbf{r},\mathbf{r}')-1]=-1. \quad (5)$$

In other words, the density $n(\mathbf{r}')[g(\mathbf{r},\mathbf{r}')-1]$ of the exchange-correlation hole around an electron at $\mathbf{r}$ represents a deficit of one electron.

The Hartree-Fock wave function $\Psi^{\mathrm{HF}}(\mathbf{r}_1\sigma_1,\ldots,\mathbf{r}_N\sigma_N)$ is the energy-optimized single-determinant approximation to Ψ, and the correlation energy is

$$E_c=\langle\Psi|\hat{H}|\Psi\rangle-\langle\Psi^{\mathrm{HF}}|\hat{H}|\Psi^{\mathrm{HF}}\rangle, \quad (6)$$

where $\hat{H}$ is the Hamiltonian. The Hartree-Fock density is often close to the true density $n(\mathbf{r})$, and for the uniform electron gas these densities are identical. For simplicity, we shall assume $n(\mathbf{r})=n^{\mathrm{HF}}(\mathbf{r})$ in the equations that follow. Then, in Hartree atomic units,

$$E_c=\int d\mathbf{r}\int d\mathbf{r}'\left(-\frac{1}{2}\nabla^2_{\mathbf{r}'}\right)[\rho_1(\mathbf{r},\mathbf{r}')-\rho_1^{\mathrm{HF}}(\mathbf{r},\mathbf{r}')] + \frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\frac{1}{|\mathbf{r}-\mathbf{r}'|}[\rho_2(\mathbf{r},\mathbf{r}')-\rho_2^{\mathrm{HF}}(\mathbf{r},\mathbf{r}')], \quad (7)$$

where the first term is the kinetic energy of correlation T_c and the second is the potential energy of correlation V_c. Moreover, for a spin-unpolarized or closed-shell system

$$\rho_2^{\mathrm{HF}}(\mathbf{r},\mathbf{r}')=n(\mathbf{r})n(\mathbf{r}')-\frac{1}{2}|\rho_1^{\mathrm{HF}}(\mathbf{r},\mathbf{r}')|^2, \quad (8)$$

$$\rho_1^{\mathrm{HF}}(\mathbf{r},\mathbf{r}')=2\sum_\alpha \psi_\alpha^{\mathrm{HF}*}(\mathbf{r}')\psi_\alpha^{\mathrm{HF}}(\mathbf{r}), \quad (9)$$

where the $\psi_\alpha^{\mathrm{HF}}(\mathbf{r})$ are the occupied Hartree-Fock orbitals.

Now we introduce the correlation contribution to the pair-distribution function

$$g_c(\mathbf{r},\mathbf{r}')=g(\mathbf{r},\mathbf{r}')-g^{\mathrm{HF}}(\mathbf{r},\mathbf{r}'). \quad (10)$$

Clearly

$$V_c=\frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\frac{n(\mathbf{r})n(\mathbf{r}')g_c(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}. \quad (11)$$

At least for the uniform gas of fixed density n, we can also write [19]

$$E_c=\frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\frac{n(\mathbf{r})n(\mathbf{r}')\overline{g_c}(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}, \quad (12)$$

$$\overline{g_c}(\mathbf{r},\mathbf{r}')=\int_0^1 d\lambda\, g_c^\lambda(\mathbf{r},\mathbf{r}'), \quad (13)$$

where g_c^λ is the correlation contribution to the pair-distribution function for electron-electron interaction $\lambda/|\mathbf{r}-\mathbf{r}'|$. The coupling constant λ varies from 0 (the Hartree-Fock wave function) to 1 (the physical wave function). Since Eq. (5) must hold for every λ (including the $\lambda=0$ or Hartree-Fock limit)

$$\int d\mathbf{r}'\, n(\mathbf{r}')g_c^\lambda(\mathbf{r},\mathbf{r}')=0. \quad (14)$$

Typically $g_c^\lambda(\mathbf{r},\mathbf{r}')$ is negative for small $u=|\mathbf{r}'-\mathbf{r}|$, and positive for large u. Comparison of Eqs. (11) and (12) with Eq. (14) then suggests that, as g_c^λ becomes more long ranged in u, it must also become deeper at small u, and E_c and V_c must become more negative. The Coulomb cusp condition, which follows from the dominance of $\lambda/|\mathbf{r}'-\mathbf{r}|$ as $\mathbf{r}'\to\mathbf{r}$, is

$$\frac{d}{du}g^\lambda(\mathbf{r},\mathbf{r}+\mathbf{u})|_{u=0}=\lambda g^\lambda(\mathbf{r},\mathbf{r}). \quad (15)$$

III. COLLE-SALVETTI APPROACH

With the concepts of the previous section in mind, consider the antisymmetric CS wave-function [1] for a spin-unpolarized system

$$\Psi^{\mathrm{CS}}(\mathbf{r}_1\sigma_1,\ldots,\mathbf{r}_N\sigma_N)=\Psi^{\mathrm{HF}}(\mathbf{r}_1\sigma_1,\ldots\mathbf{r}_N\sigma_N)\times\prod_{i>j}[1-\varphi(\mathbf{r}_i,\mathbf{r}_j)], \quad (16)$$

where

$$\varphi(\mathbf{r},\mathbf{r}')=\exp[-\beta^2(\mathbf{R})u^2]\left\{1-\Phi(\mathbf{R})\left(1+\frac{u}{2}\right)\right\} \quad (17)$$

is a Jastrow correlation factor. Here $u=|\mathbf{r}'-\mathbf{r}|$ and $\mathbf{R}=(\mathbf{r}+\mathbf{r}')/2$. Equation (17) has a cusp at $u=0$, and vanishes as $u\to\infty$. The inverse radius of the correlation hole is chosen to be

$$\beta(\mathbf{R})=qn^{1/3}(\mathbf{R}), \quad (18)$$

where $q=2.29$ from a fit of Eq. (19) of Ref. [1] to the correlation energy of the He atom. For atoms, this fit partially compensates [8] for the CS neglect of T_c and other approximations.

Having defined the CS approximation to the wave function, we must discuss the CS approximation to the correlation energy. First, Colle and Salvetti [1] assumed that $\rho_1(\mathbf{r},\mathbf{r}')=\rho_1^{\mathrm{HF}}(\mathbf{r},\mathbf{r}')$, making $T_c=0$; this is a much more doubtful approximation than the assumption $n(\mathbf{r})=n^{\mathrm{HF}}(\mathbf{r})$, as we shall see. Second, they argued that φ is small because of strong damping by the Gaussian function in Eq. (17), so that

$$\rho_2^{\mathrm{CS}}(\mathbf{r},\mathbf{r}')=\rho_2^{\mathrm{HF}}(\mathbf{r},\mathbf{r}')[1-\varphi(\mathbf{r},\mathbf{r}')]^2, \quad (19)$$

which is properly positive and satisfies the cusp condition of Eq. (15) for $\lambda=1$. The corrections to Eq. (19) that arise when φ is not small, but which vanish in two-electron systems, have been discussed by Soirat, Flocco, and Massa [20]. Thus we arrive at Eq. (9) of Ref. [1],

$$E_c^{\mathrm{CS}}=\frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\,\rho_2^{\mathrm{HF}}(\mathbf{r},\mathbf{r}')\frac{[\varphi^2(\mathbf{r},\mathbf{r}')-2\varphi(\mathbf{r},\mathbf{r}')]}{|\mathbf{r}'-\mathbf{r}|}, \quad (20)$$

which via Eq. (8) expresses the correlation energy as a functional of the Hartree-Fock one-particle density matrix.

Equation (20) is the most fundamental level of Colle-Salvetti theory, and the one tested for the uniform gas by McWeeny [5]. We note that several further approximations are made to arrive at Eq. (19) of Ref. [1], which has been used to estimate the dynamical correlation energy for molecules [2] and is the basis of the Lee-Yang-Parr density functional [3].

To complete Eq. (20), Colle and Salvetti had to find an expression for $\Phi(\mathbf{R})$ in Eq. (17). To do so, they wrote down the equation $n(\mathbf{r})-n^{\mathrm{HF}}(\mathbf{r})=0$, with $n(\mathbf{r})$ constructed from the right-hand side of Eq. (3). The result, Eq. (10) of Ref. [1], imposes the constraint of Eq. (14) for $\lambda=1$, as pointed out in Ref. [8]. However, the resulting integral equation for $\Phi(\mathbf{R})$ cannot always be solved explicitly without further approximation. Colle and Salvetti assumed that the density n varies little over the range of φ, an assumption which is error-free for the uniform gas. Thus they could have obtained an algebraic quadratic equation for $\Phi(\mathbf{R})$ (the ''full quadratic equation''), which could have been solved exactly. Instead they made a further approximation to simplify the coefficients of this quadratic equation, solved it in the high- and low-density limits, and interpolated between these limits with the simple formula

$$\Phi(\mathbf{R})=\sqrt{\pi}\beta(\mathbf{R})/[1+\sqrt{\pi}\beta(\mathbf{R})]. \tag{21}$$

IV. UNIFORM ELECTRON GAS USING EQ. (20)

Now let us consider an electron gas with a uniform density

$$n=3/(4\pi r_s^3)=k_F^3/(3\pi^2). \tag{22}$$

The Hartree-Fock pair-distribution function is

$$g^{\mathrm{HF}}(y)=1-\frac{1}{2}[3(\sin y-y\cos y)/y^3]^2, \tag{23}$$

where $y=k_F u$. The exact correlation energy per electron is

$$\epsilon_c(r_s)=t_c(r_s)+v_c(r_s)=\int_0^\infty du\, 2\pi n u\bar{g}_c(r_s,u), \tag{24}$$

where the potential energy of correlation is

$$v_c(r_s)=\int_0^\infty du\, 2\pi n u g_c(r_s,u). \tag{25}$$

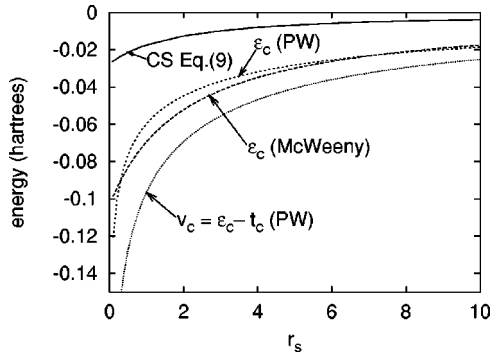

FIG. 1. Correlation energy per particle of the uniform electron gas in three dimensions, as a function of the density parameter r_s of Eq. (22). ϵ_c is the total correlation energy and v_c the potential energy of correlation. We compare Eq. (9) of CS (Ref. [1]) with McWeeny's [5] parametrization thereof and with ''exact'' PW values from Ref. [21].

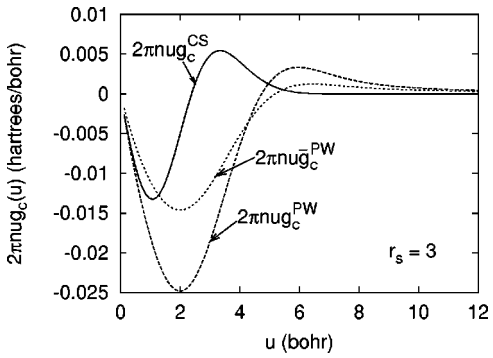

FIG. 2. Real-space analysis of the correlation energy of Fig. 1 for $r_s=3$. The area under each curve is the corresponding correlation energy, according to Eqs. (24)–(26). The ''exact'' PW values are from Ref. [14].

The functions ϵ_c and v_c are accurately known [21], as are the functions $\bar{g}_c$ and g_c [14,22,23], from a combination of theoretical constraints and diffusion Monte Carlo simulations.

The CS approximation of Eq. (20) for the uniform gas is

$$\epsilon_c^{\mathrm{CS}}(r_s)=v_c^{\mathrm{CS}}(r_s)=\int_0^\infty du\, 2\pi n u g_c^{\mathrm{CS}}(r_s,u), \tag{26}$$

$$g_c^{\mathrm{CS}}(r_s,u)=g^{\mathrm{HF}}(k_F u)[\varphi^2(r_s,u)-2\varphi(r_s,u)], \tag{27}$$

where φ is given by Eqs. (17), (18), and (21).

Figure 1 shows that ϵ_c^{CS} is only about $\frac{1}{4}$ of the true ϵ_c, and only about $\frac{1}{6}$ of the true v_c, for the range of valence electron densities $0.5\lesssim r_s\lesssim 10$. As a check of our evaluation of the integral of Eq. (26), two of us wrote independent computer programs which gave the same answer. Figure 1 also shows an analytic parametrization of ϵ_c^{CS} by McWeeny [5], which is close to ϵ_c but not to ϵ_c^{CS}.

The real-space analysis of the correlation energy is the integrand of Eq. (24) or Eq. (25), since ϵ_c is the area under the curve of $2\pi n u\bar{g}_c(r_s,u)$ vs u. For $r_s=3$, Fig. 2 compares the CS and ''exact'' real-space analyses. At small u, g_c^{CS} imitates g_c, but g_c^{CS} is of much shorter range in u than either g_c or $\bar{g}_c$.

Figure 3 shows the correlation contribution to the on-top ($u=0$) pair-distribution function, plotted as a function of r_s.

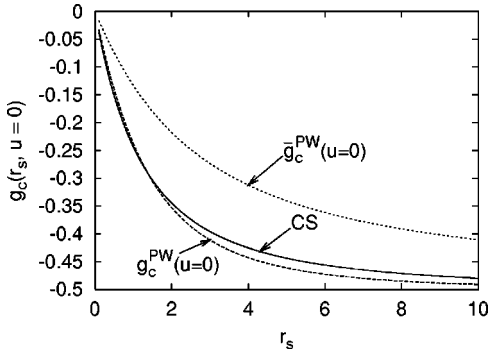

FIG. 3. On-top pair-distribution function $g_c(r_s,u=0)$ for the uniform electron gas, as a function of r_s.

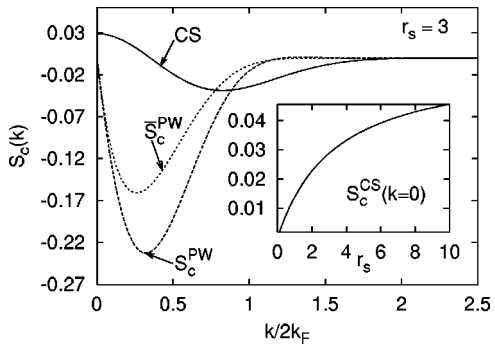

FIG. 4. Wave-vector-space analysis of the correlation energy of Fig. 1 for $r_s=3$. The area under each curve, multiplied by $2k_F/\pi$, gives the corresponding energy in hartree. The inset shows the CS violation of the sum rule of Eq. (30).

We see that $g_c^{\mathrm{CS}}(r_s,u=0)=\frac{1}{2}[\Phi^2(\mathbf{R})-1]$ imitates $g_c(r_s,u=0)$ in the high density ($r_s\to 0$) limit. Why this should be so, in view of the incorrect long-range behavior of $g_c^{\mathrm{CS}}(r_s,u)$ for the uniform electron gas, is something we do not understand. [Since in an atom $g_c(\mathbf{r},\mathbf{r})$ is determined mainly by the local spin densities at $\mathbf{r}$ [24], a roughly correct $g_c^{\mathrm{CS}}(r_s,u=0)$ might be inherited from the fit to the He atom.]

Also of interest is the Fourier transform

$$S_c(r_s,k)=\int_0^\infty du\,4\pi u^2 n g_c(r_s,u)\frac{\sin ku}{ku}. \tag{28}$$

We find

$$v_c(r_s)=\frac{1}{(2\pi)^3}\int_0^\infty dk\,4\pi k^2\frac{4\pi}{k^2}\frac{1}{2}S_c(r_s,k), \tag{29}$$

which decomposes the correlation energy into contributions from dynamic density fluctuations of various wave vectors k. Figure 4 shows the wave-vector-space analysis of the correlation energy for $r_s=3$. The large-u error of $g_c^{\mathrm{CS}}(r_s,u)$ manifests here as a small-k error.

By Eq. (14) we should find

$$\lim_{k\to 0} S_c(r_s,k)=\int_0^\infty du\,4\pi u^2 n g_c(r_s,u)=0. \tag{30}$$

The inset to Fig. 4 shows that the CS correlation does not exactly satisfy this condition, except in the limit $r_s\to 0$. In fact, the CS correlation hole contains a few hundredths of an electron. We can easily fix this problem, at least for the uniform gas, by replacing Eq. (21) by the exact solution of the full quadratic equation for Φ; this makes the CS correlation energy more negative than the CS curve in Fig. 1 (by 45% at $r_s=0$, and by 75% at $r_s=10$), but still far from the exact ϵ_c.

The most serious error in Eq. (20) for the uniform electron gas clearly arises from the strong Gaussian damping of φ in Eqs. (17) and (18). The correct long-range behavior of $g_c(r_s,u)$ in the electron gas is $\sim u^{-4}$ [14,22]. To achieve this from the wave function of Eq. (16) requires [25] that $\varphi\propto u^{-1}$ at large u. When φ decays this slowly, the justification for Eq. (19) is also lost. In fact, if $\varphi\propto u^{-1}$ at large u, then Eq. (19) would wrongly predict $g_c\propto u^{-1}$ at large u, a behavior which is not only wrong but manifestly inconsistent with Eq. (14).

In summary, key ingredients of the Colle-Salvetti functional [Eq. (9) of Ref. [1], or Eq. (20) of this article] are inappropriate to the uniform electron gas: the strong Gaussian damping in Eqs. (17) and (18), and the form of the pair density in Eq. (19). For the He atom, on the other hand, Soirat *et al.* [20] evaluated the same functional and found $E_c^{\mathrm{CS}}=-0.038$ hartree, close to the exact -0.042 hartree. Without a long-range part, the CS real-space analysis for the correlation energy (Fig. 2) cannot describe the uniform electron gas, although it describes the He atom better (Fig. 5 of Ref. [26]). While the long-range part of the CS g_c is also seriously wrong in an atom [8], this error is energetically important for the electron gas, and not for the atom (where the probability of finding two electrons far apart is very low).

V. UNIFORM ELECTRON GAS USING OTHER COLLE-SALVETTI EXPRESSIONS

Thus far, we have only been concerned with our Eq. (20) [Eq. (9) of Ref. [1] or Eq. (6.10) of Ref. [5]]. The double integral over $\mathbf{r}$ and $\mathbf{r}'$ makes evaluation of this expression cumbersome for any nonuniform density. Colle and Salvetti [1] therefore changed variables to $\mathbf{R}=(\mathbf{r}+\mathbf{r}')/2$ and $\mathbf{u}=\mathbf{r}-\mathbf{r}'$, expanded $\rho_2^{\mathrm{HF}}(\mathbf{R}-\mathbf{u}/2,\mathbf{R}+\mathbf{u}/2)\approx\frac{1}{2}n^2(\mathbf{R})[1+K(\mathbf{R})u^2/6]$, and performed the $\mathbf{u}$ integration analytically to obtain Eqs. (15) and (16) of Ref. [1], which express E_c as an integral over $\mathbf{R}$ alone of a function of $n(\mathbf{R})$ and $K(\mathbf{R})$. For the uniform electron gas, where $K=6k_F^2/5$, Eqs. (15) and (16) of Ref. [1] yield a correlation energy per electron

$$\epsilon_c=-\frac{0.02209+0.00642r_s}{1+0.79431r_s+0.1577r_s^2}, \tag{31}$$

which is very close to the ''CS Eq. (9)'' curve in our Fig. 1. Amaral and McWeeny [11] corrected Eq. (16) of Ref. [1], but the correction to Eq. (31) ($0.00642\to 0.00432$) is small.

Although Eqs. (15) and (16) of Ref. [1] seem to produce the desired simplification of Eq. (9) of Ref. [1], Colle and Salvetti replaced the function of $n(\mathbf{R})$ and $K(\mathbf{R})$ in their Eq. (16) by another function of the same variables in Eq. (19) of Ref. [1], the final form of the CS functional. The new function was chosen phenomenologically to yield a good approximation to the correlation energy density $\epsilon_c(\mathbf{R})$ of the He atom constructed from Eq. (9) of Ref. [1]. For the uniform electron gas, Eq. (19) of Ref. [1] yields a correlation energy per electron

$$\epsilon_c=-\frac{0.04918+0.01863e^{-0.40828r_s}}{1+0.56314r_s}, \tag{32}$$

which surprisingly is about twice the ''CS Eq. (9)'' curve of our Fig. 1. The Lee-Yang-Parr (LYP [3]) density functional for the correlation energy is found from Eq. (19) of Ref. [1] by making a density-gradient expansion of $K(\mathbf{R})$. Since this expansion is exact for a uniform density, Eq. (32) is also the

TABLE I. Correlation energy per electron for the uniform electron gas with density parameter $r_s=3$, exactly and in various versions of Colle-Salvetti theory.

Expression	$\epsilon_c(r_s=3)$ (hartree)
''Exact'' (Ref. [21])	−0.0370
Eq. (9) of Ref. [1]	−0.0098
Eq. (15) of Ref. [1]	−0.0086
Eq. (2.6) of Ref. [11]	−0.0073
Eq. (19) of Ref. [1]; Ref. [3]	−0.0203

LYP correlation energy for the electron gas. It is higher than the exact correlation energy by about 0.02 hartrees (Fig. 5 of Ref. [4]).

Table I compares the various CS expressions with one another and with the ''exact'' correlation energy for the electron gas with $r_s=3$. Important long-range correlations are missing in all variants of CS theory.

A correct description of the uniform electron gas is required not only for an accurate description of the solid metals [4], but also to make a correlation energy functional more transferable to a variety of systems. Some more-recent correlation energy functionals [4] that make use of $n(\mathbf{r})$ and its gradients, and sometimes of $K(\mathbf{r})$, are correct by construction for the uniform gas, accurate for atoms, and (when combined with similar exchange functionals) useful for molecular atomization energies.

The description of long-range correlation by density-functional approximations, for use with *exact* exchange, is a key problem for the future. Perhaps this problem will be solved by constructing the correlation energy from the Hartree-Fock (or Kohn-Sham) one-particle density matrix, in the same spirit but not in the same way as in the Colle-Salvetti method.

Note added in proof. A very recent critical analysis of the Colle-Salvetti functional for two-electron atoms is presented in Ref. [27].

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