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REGULAR ARTICLE

Application of the Colle–Salvetti model to the uniform electron gas

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Abstract An application of the Colle–Salvetti wave function (Colle and Salvetti in Theor Chim Acta 37: 329, 1975) to the uniform electron gas model is made. Some different levels of approximation are used. Contrarily to the previous conclusions of other work (Tao et al. in Phys Rev A 63: 032513, 2001), the present result shows that the Colle–Salvetti wave function is able to reproduce, to a semiquantitative level, the properties of the uniform electron gas. The most important request for this result is an apropiate choice for the value of the only parameter entering in the Colle–Salvetti wave function. The present results are a good complement to those obtained by Moscardó et al. (Theor Chem Accounts 115: 334, 2006) for atoms. On the basis of the results obtained in this paper, a very simple functional for the correlation energy is put forward. Its application to the uniform electron gas, lead to a very reasonable set of results. It can be concluded that the Colle–Salvetti wave function remains being a good option to built, in an approximate way, the correlation component of a N-electron system.

1 Introduction

The performance of the Colle and Salvetti (CS) wave function, or more exactly the CS two body density matrix (TBDM) [1], has been repeatedly criticized in view of its application to the ground state of the helium atom [2,3], and to the uniform electron gas [4]. All the criticisms are in the same address, namely, the CS wave function has no clear sense and the good results exhibited by the CS correlation energy formula (Eq. 10 of [1]) and other related functionals [5,6], must be explained on the basis of other reasons having no physical significance.

In a recent paper [7] it has been shown that the above assertion is wrong for the ground state of the helium atom. Properties such as sum rule, correlation potential, and the correlation energy integrand, were analyzed in [7]. The results showed that the wrong behavior founded in [3,4] for the same set of properties calculated in [7], was not due to the CS wave function but to the particular application of the first mean value theorem of the integral calculus [8] (MVT) in obtaining some of the equations appearing in [1].

In this paper the CS wave function is applied to the uniform electron gas, and the same properties as in [4] are analyzed. Similarly to the results of [7] the present results show that the CS wave function is also a reasonable good approximation to describe the uniform electron gas. Finally, as an outcome of the present analysis, a very simple density functional for the correlation energy is put forward.

2 An outline on the CS approach

The CS wave function is a Jarstrow class one [9], and it is written as

$$\Psi(\mathbf{x}_1, \ldots, \mathbf{x}_N) = \Psi^0(\mathbf{x}_1, \ldots, \mathbf{x}_N) \prod_{i \neq j}^{N} [1 - \varphi(\mathbf{r}_i, \mathbf{r}_j)] \qquad (1)$$

where $\mathbf{x}_i$ is the set of three space coordinates ($\mathbf{r}$) and the spin coordinate (m_s) of the ith electron, and Ψ^0 is a known reference wave function, usually a Hartree–Fock (HF) ones.

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For a two electron system the exact spin free TBDM associated to Eq. (1) is

$$\rho_2(\mathbf{R},\mathbf{r}) = \rho_2^0(\mathbf{R},\mathbf{r})[1+\varphi^2(\mathbf{R},\mathbf{r}) - 2\varphi(\mathbf{R},\mathbf{r})] \tag{2}$$

here ρ_2^0 is the reference TBDM corresponding to Ψ^0.

In [1] the function φ is taken as

$$\varphi(\mathbf{R},\mathbf{r}) = \exp(-\beta(\mathbf{R})^2 r^2)\left[1-\phi(\mathbf{R})\left(1+\frac{r}{2}\right)\right] \tag{3}$$

with

$$\beta(\mathbf{R}) = q\rho(\mathbf{R})^{\frac{1}{3}} \tag{4}$$

where q is a parameter, and $\rho(\mathbf{R})$ is the electron density at point $\mathbf{R}$.

In the above equations the set of coordinates

$$\mathbf{R} = \frac{\mathbf{r}_1+\mathbf{r}_2}{2} \tag{5}$$

and

$$\mathbf{r} = (\mathbf{r}_1 - \mathbf{r}_2) \tag{6}$$

is used.

If the system under consideration has more than two electrons, then Eq. (2) does not follows directly from Eq. (1). But in [1] it is supposed that this equation works also for more than two electron systems, the reason is that by invoking the MVT the Eq. (2) is also found for an N-electron system. However for the MVT apply in the integral of the product of two functions one of them must not change sign in all the rank of integration, and the other must be differentiable in the rank of integration [8]. To obtain the TBDM for the N electron wave function of Eq. (1) It must be solved the integral

$$\Gamma_2(\mathbf{r_1},\mathbf{r_2};\mathbf{r_1},\mathbf{r_2}) = \int |\Psi(\mathbf{r_1},\mathbf{r_2},\ldots,\mathbf{r_n})|^2\,\mathbf{dr_3}\ldots\mathbf{dr_n}. \tag{7}$$

It is obvious that by merely invoking the MVT when integrating Eq. (7) for $N \geq 3$, the above equation does not reduce to Eq. (2) (an approximate expression of the TBDM is found in [10]). Nevertheless for calculation purposes it seems reasonable to look at Eq. (2) as an acceptable approximation to the TBDM of an N electron atom or molecule. The uniform electron gas model refers to a very high number of electrons, and this fact may have non desirable consequences if Eq. (2) is used for approximate the TBDM. This point will be discussed further in the next sections.

The Coulomb Hole condition

$$\int \rho_2^0(\mathbf{R},\mathbf{r})[\varphi^2(\mathbf{R},\mathbf{r}) - 2\varphi(\mathbf{R},\mathbf{r})]\mathrm{d}\mathbf{r} = 0 \tag{8}$$

together the condition $\rho(\mathbf{R}) = \rho^0(\mathbf{R})$ imposes that for a normalized TBDM

$$\int \rho_2^0(\mathbf{R},\mathbf{r})[\varphi^2(\mathbf{R},\mathbf{r}) - 2\varphi(\mathbf{R},\mathbf{r})]\mathrm{d}\mathbf{R}\mathrm{d}\mathbf{r} = 0. \tag{9}$$

Although Eq. (8) fixes the $\phi(\mathbf{R})$ function that appears in Eq. (3), in the paper of CS [1] it is approximated by

$$\phi_{\mathrm{CS}}(\mathbf{R}) = \frac{\beta(\mathbf{R})\sqrt{\pi}}{1+\phi(\mathbf{R})\sqrt{\pi}}. \tag{10}$$

But it is easy to show that, under certain restrictions, the above equation can be also obtained from Eq. (8). In fact, by supposing that the MVT applies to this integral, and taking as zero the quadratic term that appears in it, Eq. (10) follows.

In [5] Eq. (8) was solved by approximating the spherically average of $\rho_2^0(\mathbf{R},\mathbf{r})$ as a Gaussian summation of the Taylor development in powers of r

$$\rho_2^0(\mathbf{R},r) = \rho_2^0(\mathbf{R},0)\exp(-\gamma(\mathbf{R})r^2). \tag{11}$$

To ensure the normalization of $\rho_2^0(\mathbf{R},r)$ the function $\gamma(\mathbf{R})$ must be

$$\gamma(\mathbf{R}) = \pi\left[\frac{(N-1)\rho^0(\mathbf{r})}{2\rho_2^0(\mathbf{R})}\right]^{-\frac{2}{3}}. \tag{12}$$

The integration of Eq. (8) with Eq. (11) lead to the $\phi_{\mathrm{MSF}}(\mathbf{R})$ function of [5], but if, as in [1], it is assumed that the quadratic term into Eq. (8) is negligeble, the following approximation is obtained

$$\phi_{\mathrm{ags}}(\mathbf{R}) = \frac{\sqrt{\pi\delta(\mathbf{R})}}{1+\sqrt{\pi\delta(\mathbf{R})}} \tag{13}$$

with

$$\delta(\mathbf{R}) = \beta^2(\mathbf{R}) + \gamma(\mathbf{R}). \tag{14}$$

Finally, a correlation energy can be written as

$$E_{\mathrm{c}} = \int \epsilon_c(\mathbf{R})\mathrm{d}\mathbf{R} \tag{15}$$

with

$$\epsilon_c(\mathbf{R}) = \frac{1}{2}\int \rho_2^0(\mathbf{R},\mathbf{r})[\varphi^2(\mathbf{R},\mathbf{r}) - 2\varphi(\mathbf{R},\mathbf{r})]\frac{\mathrm{d}\mathbf{r}}{r}. \tag{16}$$

The Eqs. (8), (9), and (16), and also the Coulomb hole

$$\rho_c(\mathbf{r}_1,\mathbf{r}_2) = \frac{\rho_2^0[\varphi^2(\mathbf{r}_1,\mathbf{r}_2) - 2\varphi(\mathbf{r}_1,\mathbf{r}_2)]}{\rho^0(\mathbf{r}_1)} \tag{17}$$

were tested in [7] for the ground state of the helium atom. The test was made by using $\phi_{\mathrm{CS}}(\mathbf{R})$, $\phi_{\mathrm{ags}}(\mathbf{R})$, and $\phi_{\mathrm{MSF}}(\mathbf{R})$ functions. The results obtained in [7] showed that the CS wave function seems to be a good approximation to the exact ones, and that the bad results reported in [2,3] must be mainly due to assuming the MVT when obtaining some key equations appearing in [1].

The question about the loss of N-representability that can appears when Eq. (2) is used for the TBDM of more than two electron systems, was also addressed in [7], concluding, on the basis of the calculations made on the helium, berilium and neon atoms, that the lack of N-representability has scarce influence on the results.

3 The uniform electron gas

In the uniform electron gas model, the density is written as

$$\rho(r_{\mathrm{s}}) = \frac{3}{4\pi r_{\mathrm{s}}^3} = \frac{k_F^3}{3\pi^2} \tag{18}$$

where r_{s} is the effective radius of a sphere containing exactly one electron.

The CS correlation component of the spherically averaged TBDM for the uniform electron gas, becomes:

$$\rho_2^c(r_{\mathrm{s}}, r) = \rho(r_{\mathrm{s}}) g^{\mathrm{HF}}(r_{\mathrm{s}}, r)[\varphi^2(r_{\mathrm{s}}, r) - 2\varphi(r_{\mathrm{s}}, r)] \tag{19}$$

where the pair distribution function is given by

$$g^{\mathrm{HF}}(r_{\mathrm{s}}, r) = 1 - \frac{[\frac{3(\sin y - y\cos y)}{y^3}]^2}{2} \tag{20}$$

with $y = k_F r$.

For the uniform electron gas Eqs. (8), (16) can be read as

$$\int_0^\infty \rho(r_{\mathrm{s}}) g^{\mathrm{HF}}(r_{\mathrm{s}}, r)[\varphi^2(r_{\mathrm{s}}, r) - 2\varphi(r_{\mathrm{s}}, r)] r^2 \mathrm{d}r = 0 \tag{21}$$

and

$$\epsilon_c(r_{\mathrm{s}}) = 2\pi \int_0^\infty \rho(r_{\mathrm{s}}) g^{\mathrm{HF}}(r_{\mathrm{s}}, r)[\varphi^2(r_{\mathrm{s}}, r) - 2\varphi(r_{\mathrm{s}}, r)] r \mathrm{d}r, \tag{22}$$

respectively.

In [4] the behavior of $\epsilon_c(r_{\mathrm{s}})$, $g^{\mathrm{HF}}(r_{\mathrm{s}}, 0)[\varphi^2(r_{\mathrm{s}}, 0) - 2\varphi(r_{\mathrm{s}}, 0)]$, and the integrand of Eq. (22), all of them taken as functions of r_{s}, was discussed by comparing with the corresponding exact functions taken from a paper of Perdew and Wang [11]. In the calculations of [4] the function $\varphi(r_{\mathrm{s}}, r)$ was built by using the $\phi_{\mathrm{CS}}(r_{\mathrm{s}})$ from Eq. (10) of this paper, together $q = 2.29$. Both sets of results discussed in [4], the exact and the approximate one, exhibited important discrepancies.

A wave-vector analysis by plotting

$$S_c(r_{\mathrm{s}}, k) = 4\pi \int_0^\infty \rho(r_{\mathrm{s}}) g^{\mathrm{HF}}(r_{\mathrm{s}}, r)[\varphi^2(r_{\mathrm{s}}, r) - 2\varphi(r_{\mathrm{s}}, r)] \times r \frac{\sin kr}{k} \mathrm{d}r \tag{23}$$

as a function of $\frac{k}{k_F}$ was also reported in [4]. The CS $S_c(r_{\mathrm{s}}, k)$ for $q = 2.29$ shows a bad behavior in all the rank of values of k, taking a wrong limit value for $k = 0$.

All the results discussed in [4] points to the existence of deep differences between the pair distribution function of CS theory and the exact ones, and on this basis it is concluded that the CS wave function, and in particular, the Eqs. (2–4), are not adequate to describe the uniform electron gas.

The results reported in [4] where all obtained by using the $\phi_{\mathrm{CS}}(r_{\mathrm{s}})$ together $q = 2.29$ (the optimum value found in [1] for the energy of the ground state of the helium atom). However, such as it was pointed in [7], the q value for a correlation hole having one electron is 1.77, very near to the optimum values found when using the $\phi_{\mathrm{MSF}}(\mathbf{R})$, and the $\phi_{\mathrm{ags}}(\mathbf{R})$ (1.70 and 1.64, respectively).

An optimum value of q for the uniform electron gas, can be obtained by imposing that, at a fixed value of r_{s}, the exact value for the correlation energy of Eq. (22), and Eq. (21) be both fulfilled. For coherence with [4], a $r_{\mathrm{s}} = 3\,au$, together the correlation energy corresponding to this point (-0.057 au), are been taken to obtain the q for the uniform electron gas. The procedure followed has been: a numerical $\phi_{\mathrm{ueg}}(r_{\mathrm{s}})$ is obtained by solving Eq. (21) for $r_{\mathrm{s}} = 3$ au, and a fixed value of q. Further, by using this set of three values, the Eq. (22) is solved. The optimum value found for q following this procedure was 1.38 , this value corresponds to about two electrons into the correlation hole, but not to the unrealistic fraction of 0.25 electron associated to $q = 2.29$. Further, by using this $q = 1.38$ and imposing that the Eq. (21) be fulfilled, a numerical function $\phi_{\mathrm{ueg}}(r_{\mathrm{s}})$ is obtained for the uniform electron gas.

Figure 1 shows the $\epsilon_c(r_{\mathrm{s}})$ of Eq. (22), obtained by using the numerical $\phi_{\mathrm{ueg}}(r_{\mathrm{s}})$. Results from $\phi_{\mathrm{CS}}(r_{\mathrm{s}})$, and $\phi_{\mathrm{MSF}}(r_{\mathrm{s}})$ together $q = 2.29$, and $q = 1.38$ are also shown in Fig. 1. In the uniform electron gas model, a very high number of electrons is asumed, hence, the functions $\phi_{\mathrm{CS}}(r_{\mathrm{s}})$, and $\phi_{\mathrm{ags}}(r_{\mathrm{s}})$, are the same, this fact is reflected in Figs. 1–4 where the results for the last function are absent. For comparison, the exact curve taken from [4] ($\epsilon_c^{\mathrm{PW}}(r_{\mathrm{s}})$) is also plotted. Such as it is reported in [4] , the CS curve with $q = 2.29$ lies above the exact ones, the same happens for the $\phi_{\mathrm{MSF}}(r_{\mathrm{s}})$ function,

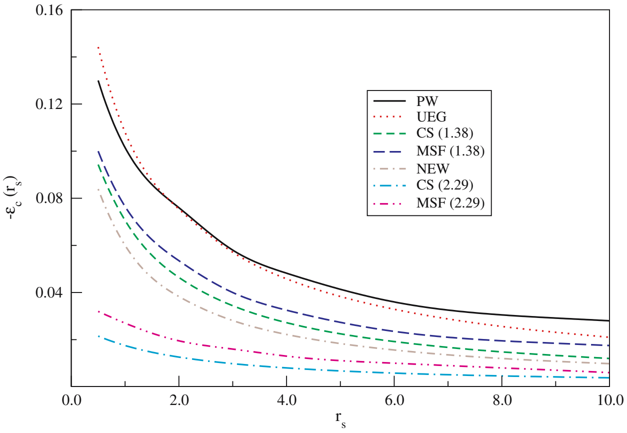

Fig. 1 Correlation energy as a function of the Wigner length

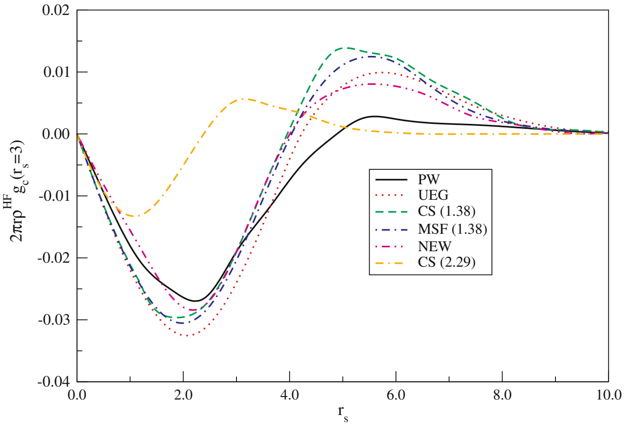

Fig. 2 Correlation energy integrand as a function of r_s

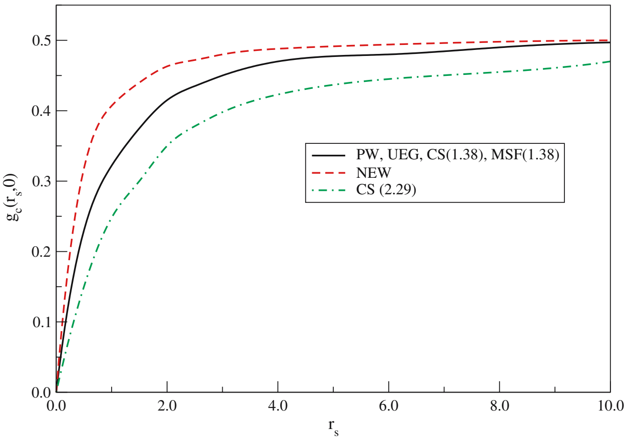

Fig. 3 On top correlation function versus Wigner length

but the curve obtained by using the $\phi_{\text{ueg}}(r_s)$ is very near to the exact ones.

The small differences found in Fig. 1 between the present results obtained with $\phi_{\text{ueg}}(r_s)$ and the exact correlation energy, are probably due to the use of a constant value for q ($q = 1.38$). If this condition is relaxed and the exact ϵ_c curve is imposed, it result in a set of values of q ranging from 1.34 to 1.4 with a mean value of 1.37, very near to that found in this paper for $r_s = 3\,au$. Three families of curves are clearly differentiated in Fig. 1, one is for CS, and MSF functions with $q = 2.29$, other is the same but with $q = 1.38$, and a third is for the PW, and ueg function together $q = 1.38$.

In Fig. 2 the $2\pi\rho(r_s) r g^{\text{HF}}(k_F r)[\varphi^2(r_s, r) - 2\varphi(r_s, r)]$ from Eq. (22) is plotted as a function of r for $r_s = 3\,au$. The exact curve is taken from [4], the other curves shown in Fig. 2 are for $\Phi_{\text{CS}}(r_s)$, $\Phi_{\text{MSF}}(r_s)$, both with $q = 2.29$, and $q = 1.38$, and $\Phi_{\text{ueg}}(r_s)(q = 1.38)$. The CS curve ($q = 2.29$) incorporates only a small fraction of the correlation energy (it integrates to $-0.0095au$), and it is concentrated into short regions of r. The uniform electron gas curve, obtained by using the $\Phi_{\text{ueg}}(r_s)$, is similar to the exact one, having both of them, extrema at approximately the same value of r. By taking $q = 1.38$, both, the CS, and the MSF curves becomes near the exact one,underlying the importance of a good choice for the parameter q.

The behavior of $g^{\text{HF}}(r_s)[\varphi^2(r_s, 0) - 2\varphi(r_s, 0)]$ furnishes information about the cusp condition for the CS wave function. Figure 3 shows, together the exact curve taken from [4], the values obtained, as a function of r_s, by using the $\phi_{\text{CS}}(r_s)$ with $q = 2.29$, the $\Phi_{\text{ueg}}(r_s)$ with $q = 1.38$, and, also, the curve for $\Phi_{\text{MSF}}(r_s)$ with $q = 1.38$. Both, the exact curve and those obtained for $q = 1.38$ are superimposed. This result reflects the fact that the CS factor of Eq. (3) includes the cusp condition for $r = 0$.

The wave-vector decomposition analysis of Eq. (24) is shown in Fig. 4. In a similar way as happens for the other properties previously discussed, the curve obtained by using the $\phi_{\text{ueg}}(r_s)$ together $q = 1.38$, is very near to the exact one [4], and it exhibits the true convergence limit for $k = 0$. This wave vector decomposition analysis has been made also for the $\Phi_{\text{CS}}(r_s, q = 2.29)$, $\Phi_{\text{CS}}(r_s, q = 1.38)$, and $\Phi_{\text{MSF}}(r_s, q = 1.38)$. The former of the three curves lies far above the exact one, the other two are very close to it.

Table 1 shows $\epsilon_c(r_s = 3\,au.)$ as a function of the number of electrons. The $\phi_{\text{ags}}(r_s)$ with $q = 1.38$ has been used for this calculations, and, for each N, the correlation energy has been optimized as a function of the parameter q. For small values of N the optimal values of $\epsilon_c(r_s)$ are far from the exact correlation energy of the uniform electron gas, but, when N becomes very high, this value is approached. This result is in accordance with the continuous nature of the uniform electron gas, and shows that the N-representability loss of Eq. (2) does not affect in a significant amount to the uniform electron gas calculations.

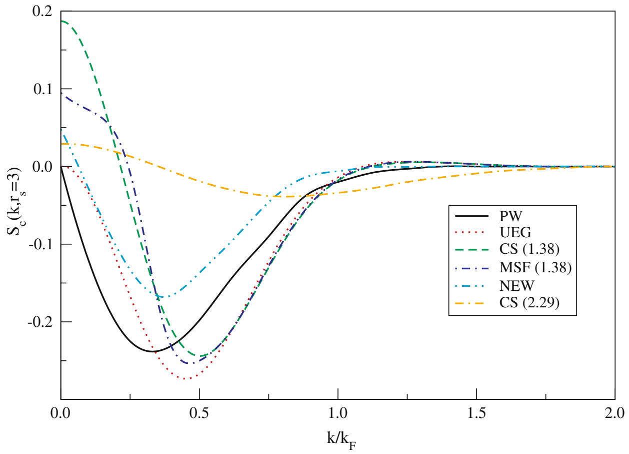

Fig. 4 Wave-vector decomposition analysis

Table 1 Correlation energy as a function of the number of electrons

N	q	ϕ	$\epsilon_c(r_s = 3\,au)$
2	3.36	0.5717	−0.0021
4	2.56	0.5010	−0.0040
6	2.28	0.4704	−0.0053
8	2.04	0.4407	−0.0066
10	1.86	0.4204	−0.0077
1,000	1.14	0.2963	−0.0557
10,000	1.16	0.2986	−0.0556
100,000	1.16	0.2984	−0.0561
1,000,000	1.16	0.2983	−0.0562

4 A very simple model

Five main conclusions are extracted from the above results: The Colle and Salvetti wave function seems to be a good choice for built the TBDM of a N electron system. The Gaussian summation works well for obtain an approximate $\phi(\mathbf{R})$. The lose of N-representability when the TBDM of Eq. (2) is used instead the exact ones has not significant effect on the results. The choice of an optimum value of q is essential for reproduce the properties of the uniform electron gas. The quadratic term appearing in Eq. (2) is of little influence wen compared with the $\varphi(\mathbf{R},\mathbf{r})$. Bearing in mind the above points, an approximate spherically averaged TBDM for the correlation contribution can be written as:

$$\rho_2^c(\mathbf{R},r) = -\rho^0(\mathbf{R},r)\varphi^c(\mathbf{R},r)\exp -\gamma(\mathbf{R})r^2 \qquad (24)$$

where $\gamma(\mathbf{R})$ is the same as in Eq. (12)

By enforcing the cusp condition on the TBDM of Eq. (24), the function $\varphi^c(\mathbf{R})$ reads as:

$$\varphi^c(\mathbf{R},r) = [1-\phi^c(\mathbf{R})(1+r)]\exp -\beta^2 r^2. \qquad (25)$$

Equation (8) is now written as:

$$\int_0^\infty [1-\phi^c(\mathbf{R}(1+r)]r^2\exp -[\delta(\mathbf{R})r^2]\mathrm{d}r = 0 \qquad (26)$$

with $\delta(\mathbf{R})$ that of Eq. (14)

From Eq. (26) it follows:

$$\Phi^c(\mathbf{R}) = \frac{\sqrt{\pi\delta(\mathbf{R})}}{2+\sqrt{\pi\delta(\mathbf{R})}}. \qquad (27)$$

Finally the correlation energy is written as

$$E_c = -1.348383\int \mathrm{d}\mathbf{R}\frac{\rho_0^2(\mathbf{R})}{\delta(\mathbf{R})[2+\sqrt{\pi\delta(\mathbf{R})}]}au. \qquad (28)$$

For the non polarized uniform electron gas the above equation reduces to the functional of the density:

$$E_c = \frac{-0.10456}{q^2}\int \mathrm{d}\mathbf{R}\frac{\rho(\mathbf{R})}{0.54977q+r_s}au \qquad (29)$$

very alike to the ancient expression obtained by Wigner for the correlation energy of the uniform electron gas [12].

The performance of Eq. (29) for the uniform electron gas has been analyzed by using now for the $g^c(r_s,r)$ of [4] the function

$$g^c(r_s,r) = -g^{\mathrm{HF}}(k_F r)\phi^c(r_s,r). \qquad (30)$$

The results obtained with this new approximation are also collected in Figs. 1–4 under the acronym NEW. All of them show an acceptable performance of the very simple Eq. (29). Theses results are obtained by using $q = 1.38$, hence, an improvement can be expected by optimizing the value of the parameter q.

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