Comment on "Communication: Simple and accurate uniform electron gas correlation energy for the full range of densities" [J. Chem. Phys. 145, 021101 (2016)]

Valentin V. Karasiev[a)]
Quantum Theory Project, Departments of Physics and of Chemistry, University of Florida, Gainesville, Florida 32611-8435, USA

(Received 2 August 2016; accepted 29 September 2016; published online 17 October 2016)

[http://dx.doi.org/10.1063/1.4964758]

Recently Chachiyo[1] presented an elegant and simple expression for the uniform electron gas (UEG) correlation energy applicable over the full range of densities. The functional has the form

$$\varepsilon_c(r_s) = a \ln\left(1 + \frac{b_1}{r_s} + \frac{b}{r_s^2}\right), \quad (1)$$

with $b_1 = b$ and r_s the usual Wigner-Seitz radius. Two sets of two parameters $\{a,b\}$ in Eq. (1) were defined for the spin-unpolarized and fully polarized cases from the requirement that Eq. (1) approaches the correlation energy of the UEG at high density (low r_s).[2] The Chachiyo functional provides a root-mean-squared error with respect to the quantum Monte-Carlo (QMC) data[3] which is a bit smaller than that provided by the Vosko-Wilk-Nusair (VWN) fit.[4]

Nevertheless, closer inspection reveals that the function deviates from the QMC data at large r_s (see Fig. 1). The relative error is equal to 8.5% at $r_s = 100$ bohrs for the spin-unpolarized case. The corresponding relative error in the *total energy* per electron is 3.5% (the reference total energy components are $t_s^{\mathrm{TF}} = 0.11$, $\varepsilon_x^{\mathrm{Slater}} = -4.58$, $\varepsilon_c^{\mathrm{Ceperley-Alder}} = -3.19$, all in mhartree).

The a and b parameters define the small-r_s behavior, while the term with b_1 contributes in the large-r_s regime. This means that if we define the b_1 parameter from a requirement to match the large-r_s QMC data, the problem of discrepancies at large-r_s may be resolved. The intermediate- and small-r_s behavior should remain essentially unchanged for small changes of b_1. Hence we propose to determine the b_1 parameter from the requirement that the correlation energy, Eq. (1), for $r_s = 50$ bohrs is equal to the QMC value. That gives the new value, $b_1 = 1.062\,717\,673 \times b = 21.739\,224\,5$ for the spin-unpolarized case and $b_1 = 1.034\,121\,079 \times b = 28.355\,973\,2$ for the fully-polarized case.

Figure 1 shows that Eq. (1) with the new b_1 parameter values provides much better agreement with the QMC data at large-r_s. There is no deterioration of the functional quality at intermediate- and small-r_s. Mean absolute relative error (MARE), maximum relative error (MAX) and mean absolute error (MAE) values for the original and revised sets of parameters are shown in Table I. For comparison, the table also includes data for the popular Perdew-Zunger (PZ)[5] and the more recently parametrized Karasiev-Sjostrom-Dufty-Trickey (KSDT)[6] *free-energy* functional evaluated at zero-temperature. Reference 7 shows that interpolation between known high- and low-density analytic limits can be used for accurate predictions of the correlation energy over the whole range of densities ($0 \le r_s < \infty$), without QMC input. Of necessity they are significantly more complicated than Eq. (1). PZ parameters were fitted to the Ceperley-Alder QMC data.[3] This functional behaves almost identically with the VWN parametrization but is more widely used, especially in solid-state codes. A subset of parameters in the KSDT functional was fitted to recent QMC results.[8] The revised parameter set should make Chachiyo's simple expression even more generally useful than the original.

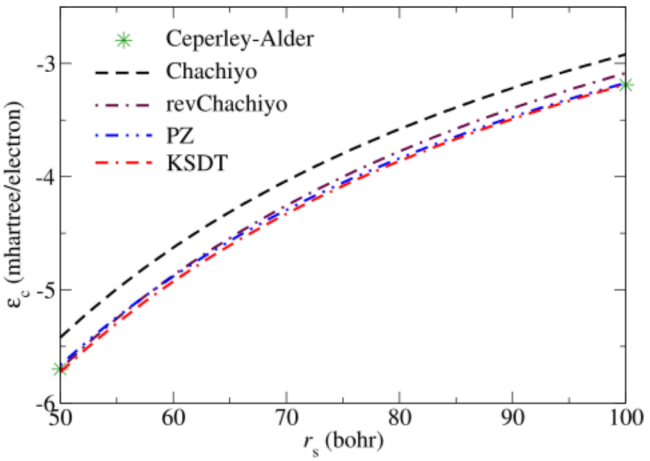

FIG. 1. Comparison among different functionals for correlation energy at large-r_s for the spin-unpolarized UEG and reference QMC data.

TABLE I. MARE (%), MAX (%) and MAE (hartrees) for the spin-unpolarized (u) and fully-polarized (p) UEG calculated with different functionals. All errors are calculated w/r to the Ceperley-Alder QMC data in the range $2 \le r_s \le 100$.

Funct.	MARE/MAX(u)	MAE(u)	MARE/MAX(p)	MAE(p)
Ref. 1	3.7/8.5	$5.4 \cdot 10^{-4}$	2.9/8.3	$1.7 \cdot 10^{-4}$
Eq. (1)	1.8/3.3	$3.2 \cdot 10^{-4}$	2.8/5.6	$2.1 \cdot 10^{-4}$
PZ	0.4/0.7	$5.2 \cdot 10^{-5}$	0.5/1.0	$3.7 \cdot 10^{-5}$
KSDT	0.9/1.5	$1.9 \cdot 10^{-4}$	2.0/5.7	$1.4 \cdot 10^{-4}$

a)Electronic address: vkarasev@qtp.ufl.edu

This work was supported by the U.S. Dept. of Energy Grant No. DE-SC0002139. Thanks to Jim Dufty and Sam Trickey for helpful discussions.

[1]T. Chachiyo, J. Chem. Phys. **145**, 021101 (2016).
[2]P. F. Loos and P. M. W. Gill, Phys. Rev. B **84**, 033103 (2011).
[3]D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980).
[4]S. H. Vosko, L. Wilk, and M. Nusair, Can. J. Phys. **58**, 1200 (1980).
[5]J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).
[6]V. V. Karasiev, T. Sjostrom, J. Dufty, and S. B. Trickey, Phys. Rev. Lett. **112**, 076403 (2014).
[7]J. Sun, J. P. Perdew, and M. Seidl, Phys. Rev. B **81**, 085123 (2010).
[8]G. G. Spink, R. J. Needs, and N. D. Drummond, Phys. Rev. B **88**, 085121 (2013).