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Critical analysis of the Colle-Salvetti wave-function functional of the density

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An analysis of the Colle-Salvetti (CS) wave-function functional of the density as applied to the He atom shows: (i) it is not normalized; (ii) the corresponding Coulomb hole structure is inaccurate; (iii) the Coulomb hole sum rule is violated; (iv) the Coulomb component of the Kohn-Sham (KS) correlation potential is inaccurate; (v) the KS correlation potential is erroneous; (vi) the Coulomb correlation and correlation-kinetic-energy components of the KS correlation energy are in error. Thus, the description by this wave function of the physics of electron correlation is inaccurate. As such the results obtained via the CS wave function and those based on it are not well founded. [S1050-2947(99)05411-6]

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The Colle-Salvetti [1] (CS) correlated-determinantal wave function, which is a functional of the density, has been widely employed [2] for the determination of the quantum chemistry definition of the correlation energy of atoms and molecules. It is an approximate parametrized form of the correlation energy expression derived via this wave function, fitted to the exact correlation energy of the He atom, that is in fact employed in the calculations. This empirical correlation energy formula has been further transformed by Lee, Yang, and Parr [3] (LYP) into a pragmatic energy functional of the density. The LYP correlation energy functional, having been incorporated into the Gaussian code [4], is possibly the most extensively used [5] functional in quantum chemistry within the context of Kohn-Sham [6] (KS) density-functional theory. In this paper we attend mainly to the CS wave function, which constitutes the underpinning of both the CS correlation energy formula as well as the LYP functional, and show that it violates several fundamental physical requirements of a wave function. It follows that results depending explicitly upon the wave function are poorly founded. (For other studies see Ref. [7].) We further point out physically meaningful results for both the quantum-chemical and KS theory definitions of the correlation energy may be determined via a correlated-determinantal-type wave-function functional provided these physical requirements are imposed. We end with a suggestion for further improving such correlated-determinantal-type wave functions.

We perform our analysis of the CS wave function as applied to the ground state of the He atom. (We employ super-scripts “CS” simply to imply quantities which logically follow from the CS wave function, even if they have not been explicitly derived or stated in the work of CS). For this atom, the CS wave function is

$$\Psi^{\text{CS}}(\mathbf{x}_1, \mathbf{x}_2) = \Phi^{\text{HF}}(\mathbf{x}_1, \mathbf{x}_2)[1 - f(\mathbf{r}_1, \mathbf{r}_2; [\rho])], \quad (1)$$

where the correlation factor

$$f(\mathbf{r}_1, \mathbf{r}_2; [\rho]) = \exp(-\beta^2 r^2)[1 - \chi(R)(1 + r/2)], \quad (2)$$

$\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$, $\mathbf{R} = (\mathbf{r}_1 + \mathbf{r}_2)/2$, $\chi(\mathbf{R}) = \sqrt{\pi}\beta/(1 + \sqrt{\pi}\beta)$, $\beta = q[\rho^{\text{HF}}(\mathbf{R})]^{1/3}$, $\Phi^{\text{HF}}(\mathbf{x}_1, \mathbf{x}_2)$ is the Hartree-Fock (HF) theory wave function, $\rho^{\text{HF}}(\mathbf{R})$ the HF density, q an empirical parameter, and $\mathbf{x} = \mathbf{r}\sigma$ with σ the spin coordinate. With $\Gamma^{\text{HF}}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2)$ and $\gamma^{\text{HF}}(\mathbf{r}_1, \mathbf{r}'_1)$ the HF theory spinless two- and one-particle density matrices, and the two-particle function $b(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2)$ defined as $b(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2) = -f(\mathbf{r}_1, \mathbf{r}_2) - f(\mathbf{r}'_1, \mathbf{r}'_2) + f(\mathbf{r}_1, \mathbf{r}_2)f(\mathbf{r}'_1, \mathbf{r}'_2)$, the expressions which may be derived from the CS wave function for the density $\rho^{\text{CS}}(\mathbf{r}_1)$, spinless single-particle density matrix $\gamma_x^{\text{CS}}(\mathbf{r}_1, \mathbf{r}'_1)$, KS theory Fermi $\rho_c^{\text{CS}}(\mathbf{r}_1, \mathbf{r}_2)$ and Coulomb $\rho_c^{\text{CS}}(\mathbf{r}_1, \mathbf{r}_2)$ hole charges are, respectively,

$$\rho^{\text{CS}}(\mathbf{r}_1) = \rho^{\text{HF}}(\mathbf{r}_1) + 2 \int \Gamma^{\text{HF}}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_1, \mathbf{r}_2) b(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2, \quad (3)$$

$$\gamma_x^{\text{CS}}(\mathbf{r}_1, \mathbf{r}'_1) = \gamma^{\text{HF}}(\mathbf{r}_1, \mathbf{r}'_1) + 2 \int \Gamma^{\text{HF}}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}_2) b(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}_2) d\mathbf{r}_2, \quad (4)$$

$$\rho_c^{\text{CS}}(\mathbf{r}_1, \mathbf{r}_2) = -|\gamma^{\text{HF}}(\mathbf{r}_1, \mathbf{r}_2)|^2/2\rho^{\text{HF}}(\mathbf{r}) \equiv -\rho^{\text{HF}}(\mathbf{r}_2)/2, \quad (5)$$

$$\rho_c^{\text{CS}}(\mathbf{r}_1, \mathbf{r}_2) = 2[\Gamma^{\text{HF}}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_1, \mathbf{r}_2) b(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_1, \mathbf{r}_2)/\rho^{\text{HF}}(\mathbf{r}_1)]. \quad (6)$$

The CS wave function gives a Coulomb energy $\mathcal{U}_c^{\text{CS}}$ which is the energy of interaction between the density and the Coulomb hole,

$$\mathcal{U}_c^{\text{CS}} = \frac{1}{2} \int \frac{\rho^{\text{HF}}(\mathbf{r}_1)\rho_c^{\text{CS}}(\mathbf{r}_1, \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2. \quad (7)$$

TABLE I. Values of the normalization integral for the Colle-Salvetti wave function as a function of the variational parameter q (in a.u.).

q	$\int \rho^{\text{CS}}(\mathbf{r}) d\mathbf{r}$
0.25	0.379 56
0.50	0.957 17
0.75	1.386 36
1.00	1.649 77
1.17	1.761 30
1.50	1.884 49
2.00	1.958 13

The KS theory correlation–kinetic energy T_c^{CS} is

$$T_c^{\text{CS}} = \frac{1}{2} \int d\mathbf{r}_1 [\nabla_{\mathbf{r}_1} \cdot \nabla_{\mathbf{r}'_1}] \Delta \gamma^{\text{CS}}(\mathbf{r}_1, \mathbf{r}'_1) |_{\mathbf{r}_1 = \mathbf{r}'_1}, \quad (8)$$

where $\Delta \gamma^{\text{CS}}(\mathbf{r}_1, \mathbf{r}'_1)$ is the correction term to $\gamma^{\text{HF}}(\mathbf{r}_1, \mathbf{r}'_1)$ of Eq. (4). The KS correlation energy $E_c^{\text{KS,CS}} = \mathcal{U}_c^{\text{CS}} + T_c^{\text{CS}}$.

We next examine the following sum rules and properties with respect to the CS wave function.

(a) *Normalization sum rule.* The normalization condition is $\int \rho(\mathbf{r}) d\mathbf{r} = N$. Substitution of the CS density Eq. (3) leads, as a function of the variational parameter q , to the results of Table I. It is evident that the CS wave function is not normalized. For large values of q , the correlation factor $f(\mathbf{r}_1, \mathbf{r}_2)$ becomes small due to the exponential term, and the normalization approaches 2 being that of the HF wave function $\Phi^{\text{HF}}(\mathbf{x}_1, \mathbf{x}_2)$. For these values of q , the CS wave function is essentially uncorrelated.

(b) *Structure of the Coulomb hole.* In Figs. 1 we compare the CS and exact [8] Coulomb hole charge distributions for different electron positions at $\mathbf{r} = 0.566, 0.8, 1.0, 1.5,$ and 5.0 a.u. The electron is assumed to be on the z -axis corresponding to $\theta = 0^\circ$. It is the cross section through the hole corresponding to $\theta' = 0^\circ$ with respect to the electron-nucleus direction that is plotted. The part of the figure corresponding to $r' < 0$ corresponds to the structure for $\theta = \pi$ and $r' > 0$. The nucleus is at the origin.

Observe that as the electron position, indicated by an arrow, is moved from inside the atom at the maximum of the radial probability density Fig. 1(a), through the atom Fig. 1(b), to the surface region Fig. 1(c), the CS Coulomb hole becomes progressively worse. (For an electron position at the nucleus, not plotted, the CS Coulomb hole is spherically symmetric as is the case of the exact hole.) In the classically forbidden Fig. 1(d) and asymptotic Fig. 1(e) regions, all similarity between the CS and exact holes vanishes. For asymptotic positions of the electron, it is derived analytically that $\lim_{r_1 \rightarrow \infty} \rho_c^{\text{CS}}(\mathbf{r}_1, \mathbf{r}_2) \sim -\rho^{\text{HF}}(\mathbf{r}_2)/2 \equiv \rho_x^{\text{HF}}(\mathbf{r}_1, \mathbf{r}_2)$. Thus, for these asymptotic positions, the CS Coulomb hole becomes the CS Fermi hole. The above remarks are reaffirmed by a comparison of the CS and exact Coulomb hole cross sections corresponding to $\theta' = 45^\circ$ and 90° . For electron positions near the nucleus, a weak cusp [9] in the CS Coulomb hole at the electron position is evident. However, this cusp is too weak to be observed even for electron positions for which the cusp in the exact hole, Figs. 1(a), 1(b), and 1(c), is clearly visible.

(c) *Coulomb hole sum rule.* According to this sum rule, the total charge of the Coulomb hole, independent of electron position, is zero:

$$\int \rho_c(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 = 0, \quad (\mathbf{r}_1 \text{ arbitrary}). \quad (9)$$

Substitution of the CS Coulomb hole into Eq. (9) leads to the results of Table II. It is evident that the sum rule is severely violated. Observe that for asymptotic positions of the electron, the total CS Coulomb hole charge approaches -1 , as it must, in light of the above discussion on the asymptotic structure of the CS hole.

(d) *Coulomb field and potential.* The Coulomb potential [10–12] $W_c(\mathbf{r})$ is the work done to move an electron in the field $\mathcal{E}_c(\mathbf{r})$ of the Coulomb hole charge

$$W_c(\mathbf{r}) = - \int_{\infty}^{\mathbf{r}} \mathcal{E}_c(\mathbf{r}') \cdot d\mathbf{l}', \quad (10)$$

where the field

$$\mathcal{E}_c(\mathbf{r}) = \int \frac{\rho_c(\mathbf{r}, \mathbf{r}') (\mathbf{r} - \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|^3} d\mathbf{r}'. \quad (11)$$

The work done is path-independent for spherically symmetric atoms, and molecules of cylindrical symmetry. Further, this potential constitutes [10] the purely Coulomb correlation component of the KS theory “exchange–correlation” and “correlation” potentials.

In Fig. 2 we compare the CS and exact [8] Coulomb fields and potentials. Although the CS field [Fig. 2(a)] vanishes at the nucleus as it must, and has the correct structure near it, its magnitude within the atom is much larger than the exact value. This is because the total CS Coulomb hole charge has a (negative) finite value. Asymptotically, the CS field decays as $O(-1/r^2)$ rather than the correct [13] $O(-1/r^5)$ structure due to the fact that the CS Coulomb hole reduces to the Fermi hole of total charge -1 for these electron positions. As expected from the structure of the CS field, the CS potential [Fig. 2(b)], has the correct structure near and at the nucleus but is about five times as large within the atom. Asymptotically, the potential decays as $O(-1/r)$ rather than the correct [13] $O(-1/r^4)$ structure. Thus, the CS Coulomb correlation component of the local potential of KS theory is substantially in error.

(e) *Kohn–Sham theory correlation potential.* The KS theory correlation potential $v_c(\mathbf{r})$ is the functional derivative $v_c(\mathbf{r}) = \delta E_c^{\text{KS}}[\rho] / \delta \rho(\mathbf{r})$, where $E_c^{\text{KS}}[\rho]$ is the KS correlation energy functional. This functional incorporates both Coulomb correlation and correlation–kinetic effects. In Fig. 3 we compare the self-consistently determined LYP correlation potential [3] with the exact result [8]. (The LYP potential employing a density determined from an accurate wave function [14] is similar). It is evident that the two potentials are quite dissimilar. The LYP functional derives from the CS functional via use of the second-order gradient expansion for the kinetic energy. For He, the *exact* kinetic energy is also given by the von Weizsäcker expression. Hence a modified Lee–Yang–Parr (M-LYP) potential may be derived by replacing the energy density of the gradient expansion in the LYP functional by the von Weizsäcker kinetic-energy-density $t_W = \frac{1}{8} |\nabla \rho(\mathbf{r})|^2 / \rho(\mathbf{r})$. The M-LYP potential is also plotted in Fig. 3. It is similar to the LYP plot, and therefore it too bears

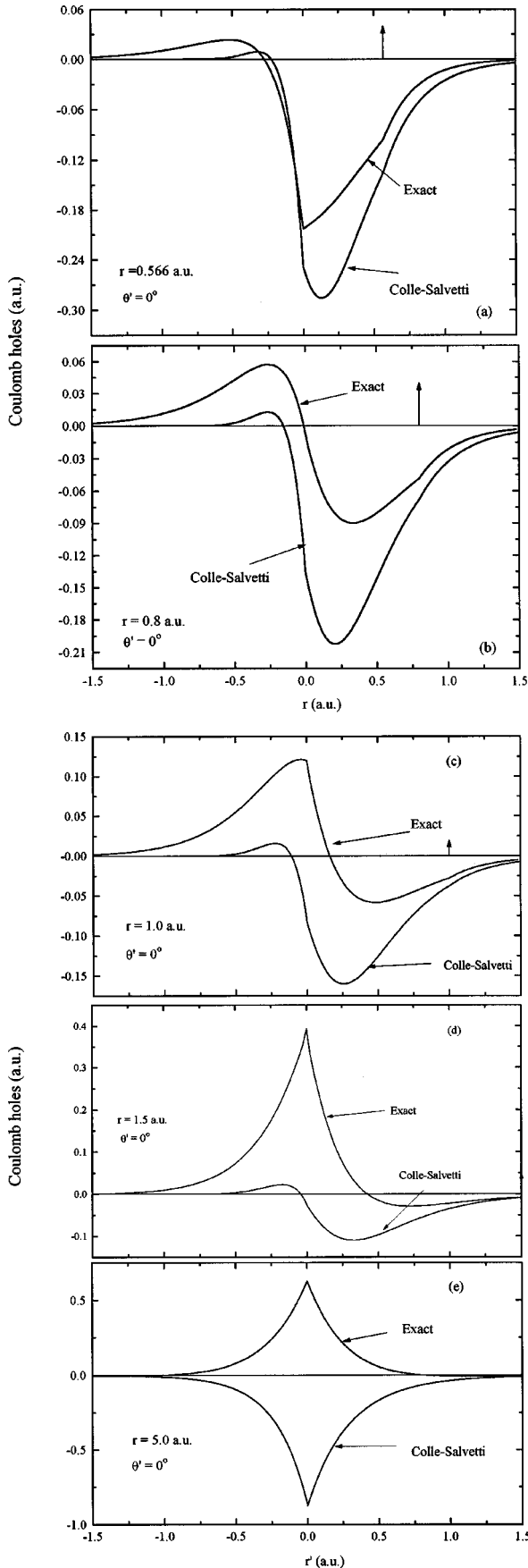


FIG. 1. The Colle-Salvetti (CS) and exact [8] Coulomb holes in a.u. for electron positions at $r=0.566, 0.8, 1.0, 1.5,$ and 5.0 a.u. The energy minimized value of the parameter $q=1.17$ is employed for the CS wave function.

TABLE II. Values of the Colle-Salvetti Coulomb hole integral at various electron positions \mathbf{r}_1 from the nucleus (in a.u.).

\mathbf{r}_1	$\int \rho_c^{\text{CS}}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2$
0.000	-0.1746
0.566	-0.1745
0.800	-0.1742
1.000	-0.1725
1.500	-0.1704
5.000	-0.5751
15.000	-0.9998

little resemblance to the exact potential. As opposed to the LYP value of E_c^{KS} of -0.0390 a.u., the M-LYP value is -0.03503 a.u., the exact value being -0.04221 a.u.

(f) *Kohn-Sham theory correlation energy and its components.* The KS correlation energy $E_c^{\text{KS}} = \mathcal{U}_c + T_c$, where \mathcal{U}_c and T_c are its Coulomb correlation and correlation-kinetic components, respectively. For the He atom, the exact values [8,14] are $E_c^{\text{KS}} = -0.04221$ a.u., $\mathcal{U}_c = -0.07875$ a.u., $T_c = 0.03664$ a.u. The results of a variational calculation [15] employing the CS wave function with q treated as a variational parameter are $E_c^{\text{KS,CS}} = -0.04307$ a.u., $\mathcal{U}_c^{\text{CS}} = -0.20975$ a.u., and $T_c^{\text{CS}} = 0.16668$ a.u. with $q=1.17$. The 150% error of $\mathcal{U}_c^{\text{CS}}$ and the over 300% error of T_c^{CS} are a consequence of the erroneous description of the physics by the CS wave function. Thus, although the correlation energy $E_c^{\text{KS,CS}}$ or the LYP E_c^{KS} are often accurate and in that sense pragmatic; none the less, there remains the deeper question of whether or not the physics of the separate components of the correlation energy are described correctly.

For the Be atom, the CS wave function with $q=2.29$ gives [16] only 3% of the KS correlation energy. A variational calculation [17] with $q=1.31$ but with the energy expression determined approximately leads to 65% of correlation energy.

The principal reason why the CS wave function is inaccurate is that the function $\chi(\mathbf{R})$ in the correlation factor $f(\mathbf{r}_1, \mathbf{r}_2)$ is determined inaccurately. CS begin by assuming $\gamma^{\text{CS}}(\mathbf{r}_1, \mathbf{r}'_1) = \gamma^{\text{HF}}(\mathbf{r}_1, \mathbf{r}'_1)$. This implies that the correction term [see Eq. (4)] $\Delta\gamma^{\text{CS}}(\mathbf{r}_1, \mathbf{r}'_1) = 0$, so that [see Eq. (8)] $T_c^{\text{CS}} = 0$ [18]. It further implies that $\rho^{\text{CS}}(\mathbf{r}_1) = \rho^{\text{HF}}(\mathbf{r}_1)$, so that the correction term [see Eq. (3)]

$$\Delta\rho^{\text{CS}}(\mathbf{r}_1) = \int \Gamma^{\text{HF}}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_1, \mathbf{r}_2) b(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 = 0. \quad (12)$$

[This condition and the Coulomb hole sum rule of Eq. (9) are equivalent.] CS determine the function $\chi(\mathbf{R})$ by satisfying Eq. (12) approximately. They first replace $\Gamma^{\text{HF}}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_1, \mathbf{r}_2)$ by $\Gamma^{\text{HF}}(\mathbf{r}_1, \mathbf{r}_1; \mathbf{r}_1, \mathbf{r}_1)$ thereby eliminating it from the equation. In the resulting quadratic equation for $\chi(\mathbf{R})$, the $\chi^2(\mathbf{R})$ term is dropped [17], and $\chi(\mathbf{R})$ determined from the linear equation. This $\chi(\mathbf{R})$ is then further approximated by the expression given below Eq. (2). Thus, the CS wave function does not satisfy Eq. (12) as demonstrated by Table I. Nor is the Coulomb hole sum rule satisfied. Nor is the assumption that $\gamma^{\text{CS}}(\mathbf{r}_1, \mathbf{r}'_1) = \gamma^{\text{HF}}(\mathbf{r}_1, \mathbf{r}'_1)$ valid.

A Taylor expansion keeping only the first term is then made by CS for the energy $\mathcal{U}_c^{\text{CS}}$ [see Eq. (7)]. With the final approximate form for the function $\chi(\mathbf{R})$ substituted into this

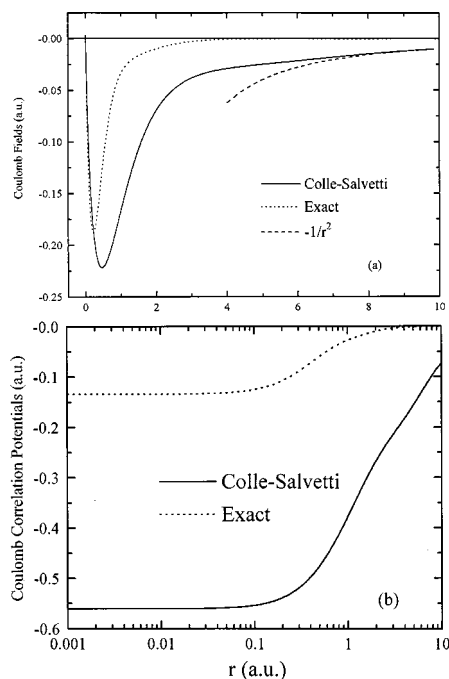


FIG. 2. Colle-Salvetti (CS) and exact [8] Coulomb fields and potentials in a.u. The energy minimized value of the parameter $q = 1.17$ is employed for the CS wave function.

expression, a Coulomb energy formula, based on the resulting equation, is developed with parameters adjusted to match the quantum-chemical correlation energy of the He atom. The LYP and M-LYP correlation energy functionals are based on this formula.

In conclusion, we have analyzed the CS wave-function functional of the density as applied to the ground state of the He atom. We note that this wave function is (i) not normalized; (ii) the structure of the Coulomb hole obtained from it is inaccurate, and for asymptotic electron positions it reduces erroneously to the KS theory Fermi hole; (iii) the CS Coulomb hole violates throughout space the sum rule on the charge distribution; (iv) it leads to a structure for the Coulomb correlation component of the KS theory correlation potential that is incorrect in magnitude; (v) the CS-KS theory correlation potential determined from the LYP functional and one obtained from a modified LYP functional valid for

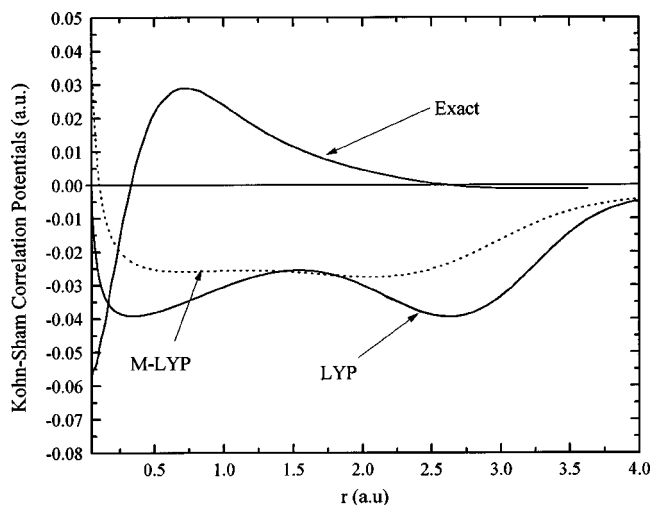


FIG. 3. The Lee-Yang-Parr (LYP), the modified M-LYP, and exact [8] KS theory correlation potentials in a.u.

the He atom bear little resemblance to the exact result, and (vi) it gives highly inaccurate values for the Coulomb correlation and correlation-kinetic-energy components of the KS correlation energy. Thus the physics of Coulomb correlations is poorly described by the CS wave function. We contend that results obtained via the wave function must be regarded with skepticism.

Finally, we note that an accurate wave-function functional of the density of correlated determinantal form may be obtained by determining the function $\chi(\mathbf{R})$ such that the condition of Eq. (12) is exactly satisfied for each electron position \mathbf{r}_1 . The sum rule on the Coulomb hole charge would simultaneously be satisfied. The orbitals of the Slater determinant part of the wave function which gives rise to the density may be improved beyond the Pauli-correlated level via the quantal description [10,11] of KS theory. In this manner, Coulomb correlation and correlation-kinetic effects *separately* derived via the correlated-determinantal wave function can be incorporated into the local effective potential, the resulting potential, orbitals, and thereby the wave-function functional being determined self-consistently. This work is in progress.

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either case. As is evident from Eqs. (7) and (8) such a separation is inherently possible. Furthermore, the Slater determinant reference state need not be Hartree-Fock, but could be based on orbitals that incorporate correlations beyond those of the Pauli exclusion principle. This would lead to an equation similar to Eq. (12) but based on orbitals that deliver the exact density [2*f*].