

Conventional Quantum Chemical Correlation Energy versus Density-Functional Correlation Energy

E.K.U. Gross, M. Petersilka and T. Grabo

Institut für Theoretische Physik, Universität Würzburg,
Am Hubland, D-97074 Würzburg, Germany

We examine the difference between the correlation energy as defined within the conventional quantum chemistry framework and its namesake in density-functional theory. Both correlation energies are rigorously defined concepts and satisfy the inequality $E_c^{\text{QC}} \geq E_c^{\text{DFT}}$. We give numerical and analytical arguments suggesting that the numerical difference between the two rigorous quantities is small. Finally, approximate density functional correlation energies resulting from some popular correlation energy functionals are compared with the conventional quantum chemistry values.

Introduction

In quantum chemistry (QC), the exact correlation energy is traditionally defined as the difference between the exact total energy and the total selfconsistent Hartree-Fock (HF) energy:

$$E_{c,\text{exact}}^{\text{QC}} := E_{\text{tot,exact}} - E_{\text{tot}}^{\text{HF}} \quad . \quad (1)$$

Within the framework of density-functional theory (DFT) [1, 2], on the other hand, the correlation energy is a functional of the density $E_c^{\text{DFT}}[\rho]$. The exact DFT correlation energy is then obtained by inserting the exact ground-state density of the system considered into the functional $E_c^{\text{DFT}}[\rho]$, i. e.

$$E_{c,\text{exact}}^{\text{DFT}} = E_c^{\text{DFT}}[\rho_{\text{exact}}] \quad . \quad (2)$$

In practice, of course, neither the quantum chemical correlation energy (1) nor the DFT correlation energy (2) are known exactly. Nevertheless, both quantities are rigorously defined concepts.

The aim of the following section is to give a coherent overview of how the correlation energy is defined in the DFT literature [3–14] and how this quantity is related to the conventional QC correlation energy. The two exact correlation energies $E_{c,\text{exact}}^{\text{QC}}$ and $E_{c,\text{exact}}^{\text{DFT}}$ are generally not identical. They satisfy the inequality $E_{c,\text{exact}}^{\text{QC}} \geq E_{c,\text{exact}}^{\text{DFT}}$. Furthermore we will give an analytical argument indicating that the difference between the two exact quantities is small.

In the last section we compare the numerical values of *approximate* conventional QC correlation energies with *approximate* DFT correlation energies resulting from some popular DFT correlation energy functionals. It turns out that the difference between DFT correlation energies and QC correlation energies is smallest for the correlation energy functional of Colle and Salvetti [15, 16] further indicating [17] that the results obtained with this functional are closest to the exact ones.

Basic Formalism

We are concerned with Coulomb systems described by the Hamiltonian

$$\hat{H} = \hat{T} + \hat{W}_{\text{C1b}} + \hat{V} \quad (3)$$

where (atomic units are used throughout)

$$\hat{T} = \sum_{i=1}^N \left(-\frac{1}{2} \nabla_i^2 \right) \quad (4)$$

$$\hat{W}_{\text{C1b}} = \frac{1}{2} \sum_{\substack{i,j=1 \\ i \neq j}}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \quad (5)$$

$$\hat{V} = \sum_{i=1}^N v(\mathbf{r}_i) \quad . \quad (6)$$

To keep the following derivation as simple as possible, we choose to work with the traditional Hohenberg-Kohn [18] formulation rather than the constrained-search representation [4, 19, 20] of DFT. In particular, all ground-state wavefunctions (interacting as well as non-interacting) are assumed to be non-degenerate. By virtue of the Hohenberg-Kohn theorem [18] the ground-state density ρ uniquely determines the external potential $v = v[\rho]$ and the ground-state wave function $\Psi[\rho]$. If $v_0(\mathbf{r})$ is a given external potential characterizing a particular physical system, the Hohenberg-Kohn total-energy functional is defined as

$$E_{v_0}[\rho] = \langle \Psi[\rho] | \hat{T} + \hat{W}_{\text{C1b}} + \hat{V}_0 | \Psi[\rho] \rangle \quad . \quad (7)$$

As an immediate consequence of the Rayleigh-Ritz principle, the total-energy functional (7) is minimized by the exact ground-state density ρ_{exact} corresponding

to the potential v_0 , the minimum value being the exact ground-state energy, i. e.

$$E_{\text{tot,exact}} = E_{v_0}[\rho_{\text{exact}}] \quad . \quad (8)$$

In the context of the Kohn-Sham (KS) scheme [21] the total-energy functional is usually written as

$$E_{v_0}[\rho] = T_s[\rho] + \int \rho(\mathbf{r})v_0(\mathbf{r}) d^3r + \frac{1}{2} \iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r d^3r' + E_{\text{xc}}[\rho] \quad (9)$$

where $T_s[\rho]$ is the kinetic-energy functional of non-interacting particles. By virtue of the Hohenberg-Kohn theorem, applied to non-interacting systems, the density ρ uniquely determines the single-particle potential $v_s[\rho]$ and the ground-state Slater-determinant

$$\Phi^{\text{KS}}[\rho] = \frac{1}{\sqrt{N!}} \det \{ \varphi_{j\sigma}^{\text{KS}}[\rho] \} \quad (10)$$

and hence $T_s[\rho]$ is given by

$$\begin{aligned} T_s[\rho] &= \langle \Phi^{\text{KS}}[\rho] | \hat{T} | \Phi^{\text{KS}}[\rho] \rangle \\ &= \sum_{\sigma=\uparrow,\downarrow} \sum_{j=1}^{N_\sigma} \int \varphi_{j\sigma}^{\text{KS}}[\rho](\mathbf{r})^* \left(-\frac{1}{2} \nabla^2 \right) \varphi_{j\sigma}^{\text{KS}}[\rho](\mathbf{r}) d^3r \quad . \end{aligned} \quad (11)$$

We mention in passing that the Hohenberg-Kohn theorem can also be formulated for a ‘‘Hartree-Fock world’’ [22], implying that the HF density uniquely determines the external potential. Consequently the HF ground-state determinant is a functional of the density as well:

$$\Phi^{\text{HF}}[\rho] = \frac{1}{\sqrt{N!}} \det \{ \varphi_{j\sigma}^{\text{HF}}[\rho] \} \quad . \quad (12)$$

The resulting kinetic-energy functional

$$\begin{aligned} T^{\text{HF}}[\rho] &= \langle \Phi^{\text{HF}}[\rho] | \hat{T} | \Phi^{\text{HF}}[\rho] \rangle \\ &= \sum_{\sigma=\uparrow,\downarrow} \sum_{j=1}^{N_\sigma} \int \varphi_{j\sigma}^{\text{HF}}[\rho](\mathbf{r})^* \left(-\frac{1}{2} \nabla^2 \right) \varphi_{j\sigma}^{\text{HF}}[\rho](\mathbf{r}) d^3r \end{aligned} \quad (13)$$

is different from $T_s[\rho]$ because the orbitals in (11) come from a *local* single-particle potential $v_s[\rho]$ while the orbitals in (13) come from the *nonlocal* HF potential $v^{\text{HF}}[\rho]$. However, the numerical difference between $T^{\text{HF}}[\rho]$ and $T_s[\rho]$ has been found to be rather small [14].

The remaining term, $E_{\text{xc}}[\rho]$, on the right hand side of equation (9) is termed the exchange-correlation (xc) energy. Comparison of equation (9) with equation (7) shows that the xc-energy functional is formally given by

$$E_{\text{xc}}[\rho] = \langle \Psi[\rho] | \hat{T} + \hat{W}_{\text{Cib}} | \Psi[\rho] \rangle - T_s[\rho] - \frac{1}{2} \iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r d^3r' \quad . \quad (14)$$

In density-functional theory the exact exchange-energy functional is defined by

$$E_x^{\text{DFT}}[\rho] := \langle \Phi^{\text{KS}}[\rho] | \hat{W}_{\text{C1b}} | \Phi^{\text{KS}}[\rho] \rangle - \frac{1}{2} \int \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r d^3r' \quad . \quad (15)$$

This is identical with the ordinary Fock functional

$$E_x^{\text{HF}}[\varphi_{j\sigma}] = -\frac{1}{2} \sum_{\sigma=\uparrow,\downarrow} \sum_{j,k=1}^{N_\sigma} \int \int d^3r d^3r' \frac{\varphi_{j\sigma}^*(\mathbf{r})\varphi_{k\sigma}^*(\mathbf{r}')\varphi_{k\sigma}(\mathbf{r})\varphi_{j\sigma}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad (16)$$

evaluated, however, with the KS Orbitals, i. e.

$$E_x^{\text{DFT}}[\rho] = E_x^{\text{HF}}[\varphi_{j\sigma}^{\text{KS}}[\rho]] \quad . \quad (17)$$

The DFT correlation-energy functional is then given by

$$E_c^{\text{DFT}}[\rho] = E_{\text{xc}}[\rho] - E_x^{\text{DFT}}[\rho] \quad . \quad (18)$$

Inserting the respective definitions (14) and (17) of $E_{\text{xc}}[\rho]$ and $E_x^{\text{DFT}}[\rho]$ we find

$$E_c^{\text{DFT}}[\rho] = \langle \Psi[\rho] | \hat{T} + \hat{W}_{\text{C1b}} | \Psi[\rho] \rangle - T_s[\rho] - \frac{1}{2} \int \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r d^3r' - E_x^{\text{HF}}[\varphi_{j\sigma}^{\text{KS}}[\rho]] \quad . \quad (19)$$

In terms of the Hartree-Fock total-energy functional

$$\begin{aligned} E_{v_0}^{\text{HF}}[\varphi_{j\sigma}] &= \sum_{\sigma=\uparrow,\downarrow} \sum_{j=1}^{N_\sigma} \int \varphi_{j\sigma}(\mathbf{r})^* \left(-\frac{1}{2} \nabla^2 \right) \varphi_{j\sigma}(\mathbf{r}) d^3r + \int \rho(\mathbf{r}) v_0(\mathbf{r}) d^3r \\ &+ \frac{1}{2} \int \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r d^3r' + E_x^{\text{HF}}[\varphi_{j\sigma}] \end{aligned} \quad (20)$$

and the total-energy functional (7) the DFT correlation energy (19) is readily expressed as

$$E_c^{\text{DFT}}[\rho] = E_{v_0}[\rho] - E_{v_0}^{\text{HF}}[\varphi_{j\sigma}^{\text{KS}}[\rho]] \quad . \quad (21)$$

By equation (2), the exact DFT correlation energy is then obtained by inserting the exact ground-state density ρ_{exact} (corresponding to the external potential v_0) into the functional (21). By virtue of equation (8) one obtains

$$E_{c,\text{exact}}^{\text{DFT}} = E_{\text{tot,exact}} - E_{v_0}^{\text{HF}}[\varphi_{j\sigma}^{\text{KS}}[\rho_{\text{exact}}]] \quad . \quad (22)$$

The conventional quantum chemical correlation energy, on the other hand, is given by

$$E_{c,\text{exact}}^{\text{QC}} = E_{\text{tot,exact}} - E_{v_0}^{\text{HF}}[\varphi_{j\sigma}^{\text{HF}}[\rho_{\text{HF}}]] \quad (23)$$

where $\varphi_{j\sigma}^{\text{HF}}[\rho_{\text{HF}}]$ are the usual selfconsistent HF orbitals corresponding to the external potential v_0 , i. e. ρ_{HF} is that very HF density which uniquely corresponds to the external potential v_0 . Of course, ρ_{HF} and ρ_{exact} are generally not identical. Comparison of (22) with (23) shows that

$$E_{c,\text{exact}}^{\text{DFT}} = E_{c,\text{exact}}^{\text{QC}} + \left(E_{v_0}^{\text{HF}}[\varphi_{j\sigma}^{\text{HF}}[\rho_{\text{HF}}]] - E_{v_0}^{\text{HF}}[\varphi_{j\sigma}^{\text{KS}}[\rho_{\text{exact}}]] \right) \quad . \quad (24)$$

This is the central equation relating the DFT correlation energy to the QC correlation energy. Since the HF orbitals $\varphi_{j\sigma}^{\text{HF}}[\rho_{\text{HF}}]$ are the ones that minimize the HF total-energy functional (20), the inequality

$$E_{v_0}^{\text{HF}}[\varphi_{j\sigma}^{\text{HF}}[\rho_{\text{HF}}]] \leq E_{v_0}^{\text{HF}}[\varphi_{j\sigma}^{\text{KS}}[\rho_{\text{exact}}]] \quad (25)$$

must be satisfied and it follows from equation (24) that

$$E_{c,\text{exact}}^{\text{QC}} \geq E_{c,\text{exact}}^{\text{DFT}} \quad . \quad (26)$$

This was first recognized by Sahni and Levy [3]. Equation (24) tells us that, as a matter of principle, selfconsistent DFT results for the correlation energy should not be compared directly with the conventional quantum chemical correlation energy but rather with the right-hand side of equation (24). In practice, of course, quantum-chemical correlation energies and ground-state densities are known only approximately, e. g. , from configuration-interaction (CI) calculations. Hence,

$$E_{\text{tot,CI}} - E_{\text{tot}}^{\text{HF}}[\varphi_{j\sigma}^{\text{KS}}[\rho_{\text{CI}}]] \quad (27)$$

is the quantity the selfconsistent DFT correlation energy should in principle be compared with. The second term of (27) is readily computed by employing one of the standard techniques [13, 23, 24, 25] of calculating the KS potential and its orbitals from a given CI density. In the following we shall argue, however, that the difference between $E_{c,\text{exact}}^{\text{DFT}}$ and $E_{c,\text{exact}}^{\text{QC}}$ can be expected to be small. To see this we rewrite equation (24) as

$$\begin{aligned} E_{c,\text{exact}}^{\text{DFT}} - E_{c,\text{exact}}^{\text{QC}} &= \left(E_{v_0}^{\text{HF}}[\varphi_{j\sigma}^{\text{HF}}[\rho_{\text{HF}}]] - E_{v_0}^{\text{HF}}[\varphi_{j\sigma}^{\text{KS}}[\rho_{\text{x-only}}]] \right) \\ &+ \left(E_{v_0}^{\text{HF}}[\varphi_{j\sigma}^{\text{KS}}[\rho_{\text{x-only}}]] - E_{v_0}^{\text{HF}}[\varphi_{j\sigma}^{\text{KS}}[\rho_{\text{exact}}]] \right) . \quad (28) \end{aligned}$$

where $\rho_{\text{x-only}}$ is the ground-state density of an exact exchange-only DFT calculation [26, 27] and $\varphi_{j\sigma}^{\text{KS}}[\rho_{\text{x-only}}]$ are the corresponding KS orbitals. The first difference on the right-hand side of equation (28) is known to be small [26, 27]. The second difference, on the other hand, is easily seen to be of *second* order in $(\rho_{\text{x-only}} - \rho_{\text{exact}})$ and is therefore expected to be small as well:

$$\begin{aligned} &E_{v_0}^{\text{HF}}[\varphi_{j\sigma}^{\text{KS}}[\rho_{\text{x-only}}]] - E_{v_0}^{\text{HF}}[\varphi_{j\sigma}^{\text{KS}}[\rho_{\text{exact}}]] \\ &= \int d^3r \left. \frac{\delta E_{v_0}^{\text{HF}}[\varphi_{j\sigma}^{\text{KS}}[\rho]]}{\delta \rho(\mathbf{r})} \right|_{\rho_{\text{x-only}}} \cdot (\rho_{\text{x-only}}(\mathbf{r}) - \rho_{\text{exact}}(\mathbf{r})) + O(\rho_{\text{x-only}} - \rho_{\text{exact}})^2 \\ &= \int d^3r \mu \cdot (\rho_{\text{x-only}}(\mathbf{r}) - \rho_{\text{exact}}(\mathbf{r})) + O(\rho_{\text{x-only}} - \rho_{\text{exact}})^2 \\ &= 0 + O(\rho_{\text{x-only}} - \rho_{\text{exact}})^2 \end{aligned}$$

The second equality follows from the fact that $\rho_{\text{x-only}}$ minimizes the density functional $E_{v_0}^{\text{HF}}[\varphi_{j\sigma}^{\text{KS}}[\rho]]$. Hence we conclude that $E_{c,\text{exact}}^{\text{DFT}} - E_{c,\text{exact}}^{\text{QC}}$ should be small. This estimate is confirmed by results of accurate variational and quantum Monte

Carlo calculations on H^- , He, Be^{+2} , Ne^{+8} [13] and Be and Ne [28] as can be seen from Table 1. There, the conventional quantum chemical correlation energies of these systems are compared with the “exact” DFT correlation energies calculated from equation (22). For all elements and ions shown, the relation (26) is confirmed, as expected. The difference between the DFT and the conventional QC correlation energies is found to be small compared with the total correlation energies. However, the absolute differences, being sometimes as high as a few mHartrees, are of the same order of magnitude as the deviations between experimental total energies and total energies calculated with *approximate* state-of-the-art density functionals [17].

Table 1: *Comparison of exact DFT correlation energies with conventional quantum chemical correlation energies (QC) [29]. Δ denotes the difference between the QC and the DFT correlation energy (in Hartree units). $\Delta\%$ denotes the value of $|E_{c,\text{exact}}^{\text{QC}} - E_{c,\text{exact}}^{\text{DFT}}|/|E_{c,\text{exact}}^{\text{DFT}}|$ in percent.*

	DFT	QC	Δ	$\Delta\%$
H^-	-0.041 995	-0.039 821	+0.002 174	5.2
He	-0.042 107	-0.042 044	+0.000 063	0.2
Be^{+2}	-0.044 274	-0.044 267	+0.000 007	0.02
Ne^{+8}	-0.045 694	-0.045 693	+0.000 001	0.002
Be	-0.096 2	-0.094 3	+0.001 9	2.0
Ne	-0.394	-0.390	+0.004	1.0

To conclude this section, we mention that there exists yet another possibility of defining a density functional for the correlation energy [4–11,13]:

$$\tilde{E}_c[\rho] = E_{v_0}[\rho] - E_{v_0}^{\text{HF}}[\varphi_{j\sigma}^{\text{HF}}[\rho]] \quad (29)$$

where $\varphi_{j\sigma}^{\text{HF}}[\rho]$ are the HF orbitals corresponding to the density ρ (see equation (12)). If the exact density ρ_{exact} is inserted in (29) $\varphi_{j\sigma}^{\text{HF}}[\rho_{\text{exact}}]$ are the HF orbitals corresponding to some unknown external potential \tilde{v}_0 whose HF density is ρ_{exact} . The decomposition

$$\tilde{v}_0(\mathbf{r}) =: v_0(\mathbf{r}) + \tilde{v}_c(\mathbf{r}) \quad (30)$$

makes clear that on the single-particle level the definition (29) leads to a hybrid scheme featuring the ordinary *non-local* HF exchange potential combined with the *local* correlation potential $\tilde{v}_c(\mathbf{r})$. In the present paper, this hybrid scheme will not be further investigated. We only mention that, with arguments similar to the one leading to (26) \tilde{E}_c satisfies the inequalities:

$$\tilde{E}_c[\rho_{\text{exact}}] \leq E_{c,\text{exact}}^{\text{QC}} \leq \tilde{E}_c[\rho_{\text{HF}}] \quad (31)$$

as was first pointed out by Savin, Stoll and Preuss [8].

Correlation Energies from Various DFT Approximations

For further analysis, we compare in Tables 2, 3 and 4 the DFT correlation energies resulting from various approximations to $E_c^{\text{DFT}}[\rho]$. LYP denotes the correlation-energy functional by Lee, Yang and Parr [30], PW91 the generalized gradient approximation by Perdew and Wang [31], and LDA the conventional local density approximation in the parametrisation of E_c by Vosko, Wilk and Nusair [32]. The first column, denoted by CS and KLI-CS, respectively, shows the results of a recently developed scheme which employs an optimized effective potential (OEP) including correlation effects [17]. In this scheme the full integral equation of the optimized effective potential method [33, 34],

$$\sum_{i=1}^{N_\sigma} \int d^3 r' \left(V_{\text{xc}\sigma}^{\text{OEP}}(\mathbf{r}') - u_{\text{xc}i\sigma}(\mathbf{r}') \right) \left(\sum_{\substack{k=1 \\ k \neq i}}^{\infty} \frac{\varphi_{k\sigma}^*(\mathbf{r}) \varphi_{k\sigma}(\mathbf{r}')}{\varepsilon_{k\sigma} - \varepsilon_{i\sigma}} \right) \varphi_{i\sigma}(\mathbf{r}) \varphi_{i\sigma}^*(\mathbf{r}') + c.c. = 0 \quad (32)$$

with

$$u_{\text{xc}i\sigma}(\mathbf{r}) := \frac{1}{\varphi_{i\sigma}^*(\mathbf{r})} \frac{\delta E_{\text{xc}}[\varphi_{j\sigma}]}{\delta \varphi_{i\sigma}(\mathbf{r})} \quad (33)$$

is solved semi-analytically by an approved method due to Krieger, Li and Iafrate [35, 36, 37]:

$$V_{\text{xc}\sigma}^{\text{OEP}}(\mathbf{r}) \approx V_{\text{xc}\sigma}^{\text{KLI}}(\mathbf{r}) = \frac{1}{\rho_\sigma(\mathbf{r})} \sum_{i=1}^{N_\sigma} \rho_{i\sigma}(\mathbf{r}) \left[u_{\text{xc}i\sigma}(\mathbf{r}) + \left(\bar{V}_{\text{xc}i\sigma}^{\text{KLI}} - \bar{u}_{\text{xc}i\sigma} \right) \right] \quad (34)$$

where the constants $\left(\bar{V}_{\text{xc}i\sigma}^{\text{KLI}} - \bar{u}_{\text{xc}i\sigma} \right)$ are the solutions of the set of linear equations

$$\sum_{i=1}^{N_\sigma-1} (\delta_{ji} - M_{ji\sigma}) \left(\bar{V}_{\text{xc}i\sigma}^{\text{KLI}} - \bar{u}_{\text{xc}i\sigma} \right) = \bar{V}_{\text{xc}j\sigma}^{\text{S}} - \bar{u}_{\text{xc}j\sigma} \quad j = 1, \dots, N_\sigma \quad (35)$$

with

$$M_{ji\sigma} := \int d^3 r \frac{\rho_{j\sigma}(\mathbf{r}) \rho_{i\sigma}(\mathbf{r})}{\rho_\sigma(\mathbf{r})}, \quad (36)$$

$$V_{\text{xc}\sigma}^{\text{S}}(\mathbf{r}) := \sum_{i=1}^N \frac{\rho_{i\sigma}(\mathbf{r})}{\rho_\sigma(\mathbf{r})} u_{\text{xc}i\sigma}(\mathbf{r}). \quad (37)$$

Here, $\bar{u}_{\text{xc}j\sigma}$ denotes the average value of $u_{\text{xc}j\sigma}(\mathbf{r})$ taken over the density of the $j\sigma$ orbital, i. e.

$$\bar{u}_{\text{xc}j\sigma} = \int \rho_{j\sigma}(\mathbf{r}) u_{\text{xc}j\sigma}(\mathbf{r}) d^3 r \quad (38)$$

and similarly for $\bar{V}_{\text{xc}j\sigma}^{\text{S}}$. Like in the conventional Kohn-Sham method, the xc-potential resulting from equation (34) leads to a single-particle Schrödinger equation with a *local* effective potential

$$\left(-\frac{\nabla^2}{2} + v_0(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3 r' + V_{\text{xc}\sigma}^{\text{OEP}}(\mathbf{r}) \right) \varphi_{j\sigma}(\mathbf{r}) = \varepsilon_{j\sigma} \varphi_{j\sigma}(\mathbf{r}) \quad (39)$$

$(j = 1, \dots, N_\sigma \quad \sigma = \uparrow, \downarrow).$

The selfconsistent solutions $\varphi_{j\sigma}(\mathbf{r})$ of equation (39) with lowest single-particle energies $\varepsilon_{j\sigma}$ minimize the total-energy functional

$$\begin{aligned}
E_{v_0}^{\text{OEP}}[\varphi_{j\sigma}] &= \sum_{\sigma=\uparrow,\downarrow} \sum_{i=1}^{N_\sigma} \int \varphi_{i\sigma}^*(\mathbf{r}) \left(-\frac{1}{2}\nabla^2\right) \varphi_{i\sigma}(\mathbf{r}) d^3r \\
&+ \int \rho(\mathbf{r}) v_0(\mathbf{r}) d^3r \\
&+ \frac{1}{2} \iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3r d^3r' \\
&- \frac{1}{2} \sum_{\sigma=\uparrow,\downarrow} \sum_{j,k=1}^{N_\sigma} \iint d^3r d^3r' \frac{\varphi_{j\sigma}^*(\mathbf{r})\varphi_{k\sigma}^*(\mathbf{r}')\varphi_{k\sigma}(\mathbf{r})\varphi_{j\sigma}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \\
&+ E_c^{\text{CS}}[\{\varphi_{j\sigma}\}]. \tag{40}
\end{aligned}$$

In the above equation, E_c^{CS} denotes the Colle-Salvetti functional [15, 16] for the correlation-energy given by

$$\begin{aligned}
E_c^{\text{CS}} &= -ab \int \gamma(\mathbf{r})\xi(\mathbf{r}) \left[\sum_\sigma \rho_\sigma(\mathbf{r}) \sum_i |\nabla\varphi_{i\sigma}(\mathbf{r})|^2 - \frac{1}{4} |\nabla\rho(\mathbf{r})|^2 \right. \\
&\quad \left. - \frac{1}{4} \sum_\sigma \rho_\sigma(\mathbf{r})\Delta\rho_\sigma(\mathbf{r}) + \frac{1}{4}\rho(\mathbf{r})\Delta\rho(\mathbf{r}) \right] d^3r \\
&- a \int \gamma(\mathbf{r}) \frac{\rho(\mathbf{r})}{\eta(\mathbf{r})} d^3r, \tag{41}
\end{aligned}$$

where

$$\gamma(\mathbf{r}) = 4 \frac{\rho_\uparrow(\mathbf{r})\rho_\downarrow(\mathbf{r})}{\rho(\mathbf{r})^2}, \tag{42}$$

$$\eta(\mathbf{r}) = 1 + d\rho(\mathbf{r})^{-\frac{1}{3}}, \tag{43}$$

$$\xi(\mathbf{r}) = \frac{\rho(\mathbf{r})^{-\frac{5}{3}} e^{-c\rho(\mathbf{r})^{-\frac{1}{3}}}}{\eta(\mathbf{r})}. \tag{44}$$

The constants a , b , c and d are given by

$$\begin{aligned}
a &= 0.04918, & b &= 0.132, \\
c &= 0.2533, & d &= 0.349.
\end{aligned}$$

In Table 2, the four *approximate* DFT correlation energy functionals are evaluated at the exact densities [13, 28] of H^- , He, Be^{+2} , Ne^{+8} , Be, Ne and compared with the *exact* DFT correlation energies given by equation (22). On average, the KLI-CS values are superior.

In Table 3 selfconsistent DFT correlation energies are compared with QC values taken from [38]. In these selfconsistent calculations the *approximate* correlation-energy functionals E_c^{LYP} , E_c^{PW91} , E_c^{LDA} are complemented with the *approximate* exchange-energy functionals E_x^{B88} [39], E_x^{PW91} [31] and E_x^{LDA} , respectively. In the KLI-CS case, the DFT exchange-energy functional (17) is of course treated exactly. The numerical data show three main features:

Table 2: Non-relativistic absolute correlation energies resulting from various approximate DFT correlation energy functionals, evaluated at the exact ground-state densities [13, 28] of the respective atoms (in Hartree units). Exact values are from [13, 38]. $|\Delta|\%$ denotes the mean value of $|E_c - E_{c,\text{exact}}^{\text{DFT}}|/|E_{c,\text{exact}}^{\text{DFT}}|$ in percent.

	CS	LYP	PW91	LDA	EXACT
H ⁻	0.0297	0.0299	0.0320	0.0718	0.0420
He	0.0416	0.0438	0.0457	0.1128	0.0421
Be ⁺²	0.0442	0.0491	0.0535	0.1512	0.0443
Ne ⁺⁸	0.0406	0.0502	0.0617	0.2030	0.0457
Be	0.0936	0.0955	0.0950	0.2259	0.0962
Ne	0.375	0.383	0.381	0.745	0.394
$ \Delta \%$	8.2	9.5	15.4	175	

Table 3: Non-relativistic absolute correlation energies of first and second row atoms from selfconsistent calculations with various DFT approximations. QC denotes the conventional quantum chemistry value [38]. $|\Delta|\%$ denotes the mean value of $|(E_c^{\text{DFT}} - E_c^{\text{QC}})/E_c^{\text{QC}}|$ in percent. All other numbers in Hartree units.

	KLI-CS	BLYP	PW91	LDA	QC
He	0.0416	0.0437	0.0450	0.1115	0.0420
Li	0.0509	0.0541	0.0571	0.1508	0.0453
Be	0.0934	0.0954	0.0942	0.2244	0.0943
B	0.1289	0.1287	0.1270	0.2906	0.1249
C	0.1608	0.1614	0.1614	0.3587	0.1564
N	0.1879	0.1925	0.1968	0.4280	0.1883
O	0.2605	0.2640	0.2587	0.5363	0.2579
F	0.3218	0.3256	0.3193	0.6409	0.3245
Ne	0.3757	0.3831	0.3784	0.7434	0.3905
Na	0.4005	0.4097	0.4040	0.8041	0.3956
Mg	0.4523	0.4611	0.4486	0.8914	0.4383
Al	0.4905	0.4979	0.4891	0.9661	0.4696
Si	0.5265	0.5334	0.5322	1.0418	0.5050
P	0.5594	0.5676	0.5762	1.1181	0.5403
S	0.6287	0.6358	0.6413	1.2259	0.6048
Cl	0.6890	0.6955	0.7055	1.3289	0.6660
Ar	0.7435	0.7515	0.7687	1.4296	0.7223
$ \Delta \%$	3.13	4.52	5.10	120	

Table 4: *Non-relativistic absolute correlation energies of atoms from selfconsistent calculations with various DFT approximations. All numbers in Hartree units.*

	KLI-CS	BLYP	PW91		KLI-CS	BLYP	PW91
K	0.8030	0.7821	0.7994	Rb	1.7688	1.7832	1.9509
Ca	0.8269	0.8329	0.8467	Sr	1.8222	1.8355	2.0056
Sc	0.8832	0.8855	0.9033	Y	1.8763	1.8863	2.0671
Ti	0.9371	0.9374	0.9613	Zr	1.9281	1.9363	2.1307
V	0.9882	0.9882	1.0198	Nb	1.9475	1.9558	2.1899
Cr	1.0073	1.0086	1.0736	Mo	1.9905	2.0003	2.2551
Mn	1.0812	1.0861	1.1375	Tc	2.0796	2.0874	2.3412
Fe	1.1597	1.1620	1.2158	Ru	2.1571	2.1637	2.4254
Co	1.2324	1.2331	1.2933	Rh	2.2278	2.2340	2.5081
Ni	1.3009	1.3010	1.3700	Pd	2.3123	2.3154	2.6074
Cu	1.3693	1.3694	1.4562	Ag	2.3561	2.3649	2.6705
Zn	1.4273	1.4303	1.5212	Cd	2.4146	2.4247	2.7373
Ga	1.4704	1.4753	1.5768	In	2.4600	2.4704	2.7964
Ge	1.5101	1.5174	1.6343	Sn	2.5024	2.5135	2.8577
As	1.5465	1.5570	1.6917	Sb	2.5419	2.5544	2.9193
Se	1.6177	1.6288	1.7662	Te	2.6134	2.6252	2.9965
Br	1.6795	1.6912	1.8393	I	2.6763	2.6876	3.0726
Kr	1.7355	1.7493	1.9112	Xe	2.7338	2.7456	3.1475

1. For most atoms, the absolute value of E_c^{QC} is smaller than the absolute correlation energy obtained with any DFT method, as it should be according to the relation (26).
2. The values of $E_c^{\text{KLI-CS}}$, E_c^{LYP} , E_c^{PW91} and E_c^{QC} agree quite closely with each other while the absolute value of E_c^{LDA} is too large roughly by a factor of two. We mention that due to the well known error cancellation between E_x^{LDA} and E_c^{LDA} , the resulting LDA values for total xc energies are much better.
3. The difference between E_c^{DFT} and E_c^{QC} is smallest for the $E_c^{\text{KLI-CS}}$ values, larger for E_c^{LYP} and largest for E_c^{PW91} . The difference between E_c^{QC} and E_c^{DFT} has three sources:
 - (a) The values of E_c^{QC} are only approximate, i. e. not identical with $E_{c,\text{exact}}^{\text{QC}}$.
 - (b) The values of E_c^{DFT} are only approximate, i. e. not identical with $E_{c,\text{exact}}^{\text{DFT}}$.
 - (c) As shown in the last section, the exact values $E_{c,\text{exact}}^{\text{QC}}$ and $E_{c,\text{exact}}^{\text{DFT}}$ are not identical.

Currently it is not known with certainty which effect gives the largest contribution. However, with the arguments given in the last section, we expect the contribution of (c) to be small. Assuming that the quoted values of E_c^{QC} are very close to $E_{c,\text{exact}}^{\text{QC}}$ we conclude that $E_c^{\text{KLI-CS}}$ is closest to $E_{c,\text{exact}}^{\text{DFT}}$.

Table 4 shows correlation energies of atoms K through Xe obtained with the various selfconsistent DFT approaches. In almost all cases, the absolute KLI-CS values for E_c are smallest and the ones from PW91 are largest, while the LYP values lie in between. In most cases, $E_c^{\text{KLI-CS}}$ and E_c^{BLYP} agree within less than 1 % while $|E_c^{\text{PW91}}|$ is larger (by up to 10 %) as the atomic number Z increases. We emphasize that reliable values for E_c^{QC} do not exist for these atoms.

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