

Connections between the correlation potential and the static correlation kernel for two-electron densities in high-density limit

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Abstract

New approximations with improved shapes of their corresponding potentials are especially needed for high-quality Kohn–Sham calculations. For two-electron densities, a new exact expression for the correlation potential $v_c([n]; \mathbf{r})$ in its high-density scaling limit is derived. Our formula links $v_c([n]; \mathbf{r})$ to an integral of the static correlation kernel $f_c([n]; \mathbf{r}, \mathbf{r}')$, $f_c([n]; \mathbf{r}, \mathbf{r}') = \delta v_c([n]; \mathbf{r}) / \delta n(\mathbf{r}')$, in the high-density limit. Numerical results, both exact and approximate, for $\iint f_c([n]; \mathbf{r}, \mathbf{r}') n(\mathbf{r}) n(\mathbf{r}') d\mathbf{r} d\mathbf{r}'$ in the high-density limit for two model two-electron densities, are presented. It is shown that several popular functionals give the wrong sign for the latter. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction and definitions

Density functional theory (DFT) [1–11] has provided an effective methodology for quantum chemistry calculations. The most widely used implementation of the present density functional formalism is Kohn–Sham (KS) theory [2–5]. In this theory, the interacting system of interest is replaced by a model non-interacting system with the same ground-state density in a new effective potential (the KS potential) incorporating all effects associated with the electron–electron interactions. The ground-state properties are obtained from the non-interacting KS wavefunction and its corresponding density which, in turn, is the true ground-state density of the interacting system. Other properties like the polarizability, hyperpolarizability, and excitation energies are calcu-

lated by means of the time-dependent KS approach [9–11] via the non-interacting KS response function.

In density functional calculations an energy functional must be employed. The exact form of the exchange–correlation component $E_{xc}[n]$ of this functional is unknown and has to be approximated. For convenience, $E_{xc}[n]$ is further partitioned into exchange, $E_x[n]$, and correlation, $E_c[n]$, contributions, i.e. $E_{xc}[n] = E_x[n] + E_c[n]$ [8]. In order to arrive at the very best approximations to $E_x[n]$ and $E_c[n]$, knowledge of their exact properties is needed. One of the most powerful approaches for studying the exact properties of the unknown $E_x[n]$ and $E_c[n]$ is the coordinate scaling of the density. Upon uniform scaling of the density given by

$$n_\lambda(x, y, z) \equiv \lambda^3 n(\lambda x, \lambda y, \lambda z), \quad (1)$$

the following simple scaling occurs with $E_x[n]$, [8]:

$$E_x[n_\lambda] = \lambda E_x[n], \quad (2)$$

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where the exchange energy functional $E_x[n]$ is defined as

$$E_x[n] = \langle \Phi_0[n] | \hat{V}_{ee} | \Phi_0[n] \rangle - U[n]. \quad (3)$$

In Eq. (3), \hat{V}_{ee} is the electron–electron repulsion operator, and $\Phi_0[n]$ is the KS wavefunction, i.e. the wavefunction that minimizes the expectation value of the kinetic energy operator and yields the density $n(\mathbf{r})$. Except for certain degenerate cases, $\Phi_0[n]$ is a single determinant [12]. The Hartree electron–electron repulsion energy component, $U[n]$, is known explicitly in terms of the density, and is given by

$$U[n] = \frac{1}{2} \iint \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'. \quad (4)$$

For computational purposes, $E_x[n]$ is often approximated as an explicit functional of the density, even though it is known exactly in terms of the KS wavefunction. The explicit functional dependence of $E_x[n]$ on $n(\mathbf{r})$ is known only for two-electron diamagnetic densities because $E_x[n] = (-\frac{1}{2})U[n]$.

The correlation energy functional, $E_c[n]$, which contains all complicated dimensionality when $n(\mathbf{r})$ is scaled uniformly, is given by

$$E_c[n] = \langle \Psi[n] | \hat{T} + \hat{V}_{ee} | \Psi[n] \rangle - \langle \Phi_0[n] | \hat{T} + \hat{V}_{ee} | \Phi_0[n] \rangle, \quad (5)$$

where \hat{T} is the kinetic energy operator, and $\Psi[n]$ is that antisymmetric wavefunction that minimizes $\langle \hat{T} + \hat{V}_{ee} \rangle$ and yields the density $n(\mathbf{r})$. Upon uniform scaling of the density, $E_c[n]$ does not scale homogeneously. Instead, it satisfies the following high- λ (high-density) scaling limit [13–17]

$$\lim_{\lambda \rightarrow \infty} E_c[n_\lambda] = E_c^{(2)}[n], \quad (6)$$

where $E_c^{(2)}[n]$ is the leading second-order contribution to the correlation energy $E_c[n]$ for any trial density $n(\mathbf{r})$.

The quantity $2E_c^{(2)}[n]$ is particularly important because it is the initial slope [14] in the adiabatic connection method (coupling-constant formula) for $E_c[n]$ [13,14,18–26]. It is also believed that $E_c[n]$ is relatively insensitive to coordinate scaling [14,17], i.e. $E_c^{(2)}[n] \sim E_c[n]$ for small atoms. As a result, knowledge of $E_c^{(2)}[n]$ can be used for constructing accurate approximations to $E_c[n]$.

The quality of the KS calculations depends on properties of the approximations used to generate the KS potential. The KS potential $v_s([n]; \mathbf{r})$ is a unique functional of the density $n(\mathbf{r})$, and is written as

$$v_s([n]; \mathbf{r}) = v(\mathbf{r}) + u([n]; \mathbf{r}) + v_x([n]; \mathbf{r}) + v_c([n]; \mathbf{r}), \quad (7)$$

where $v(\mathbf{r})$ is the physical external potential of the system. The Hartree potential $u([n]; \mathbf{r})$ is

$$u([n]; \mathbf{r}) = \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}', \quad (8)$$

which is the functional derivative of the Hartree electron–electron repulsion energy $U[n]$. In Eq. (8), the exchange potential $v_x([n]; \mathbf{r})$ is the functional derivative of $E_x[n]$ with respect to $n(\mathbf{r})$, i.e. $v_x([n]; \mathbf{r}) = \delta E_x[n] / \delta n(\mathbf{r})$, and $v_c([n]; \mathbf{r})$ is the correlation potential defined as the functional derivative of $E_c[n]$, i.e. $v_c([n]; \mathbf{r}) = \delta E_c[n] / \delta n(\mathbf{r})$.

When the time-dependent KS formalism within the adiabatic approximation is invoked, one needs functionals which not only produce good potentials, but also yield reliable results for the static (zero-frequency) exchange and correlation kernels. The static exchange kernel $f_x([n]; \mathbf{r}, \mathbf{r}')$ and the static correlation kernel $f_c([n]; \mathbf{r}, \mathbf{r}')$ are defined respectively by

$$f_x([n]; \mathbf{r}, \mathbf{r}') = \frac{\delta v_x([n]; \mathbf{r})}{\delta n(\mathbf{r}')}, \quad (9a)$$

and

$$f_c([n]; \mathbf{r}, \mathbf{r}') = \frac{\delta v_c([n]; \mathbf{r})}{\delta n(\mathbf{r}')}. \quad (9b)$$

The correlation potential, $v_c([n]; \mathbf{r})$, is very difficult to approximate and many approximations to $E_c[n]$ yielding very accurate results for the correlation energy fail to produce good potentials. The static correlation kernel, $f_c([n]; \mathbf{r}, \mathbf{r}')$, is even more difficult to mimic due to its response nature in contrast to $v_c([n]; \mathbf{r})$ being a point-wise expression, and $E_c[n]$ being just a number. While there are many exact conditions on $E_c[n]$ to guide construction of approximations, relatively few exist for $v_c([n]; \mathbf{r})$ and $f_c([n]; \mathbf{r}, \mathbf{r}')$. It is with this in mind, that we derive a new expression, Eq. (22), for the

high-density scaling limit of $v_c([n]; \mathbf{r})$ for two-electron densities in terms of $f_c([n]; \mathbf{r}, \mathbf{r}')$. Connections with previously derived results are established. Numerical tests for $\int f_c([n]; \mathbf{r}, \mathbf{r}') n(\mathbf{r}') n(\mathbf{r}) d\mathbf{r}' d\mathbf{r}$, in the high-density scaling limit for model two-electron densities, are presented. The exact numbers are compared with results from viable approximations to $E_c[n]$.

2. Derivations

The link between uniform scaling of the electron density and scaling of the electron–electron interaction in the adiabatic connection has been developed by Görling and Levy [14,23–25]. The effective potential and the scaled electron–electron interaction along the coupling constant path, which connects a non-interacting and a fully interacting system with the same electron density, have been used to construct a DFT perturbation theory. A key result from this perturbation theory [14,23–25] is the identification of $E_c^{(2)}[n]$ as

$$E_c^{(2)}[n] = \frac{1}{2} \left\{ \langle \Phi_0[n] | \hat{H}^{(1)}[n] | \Psi^{(1)}[n] \rangle + \langle \Psi^{(1)}[n] | \hat{H}^{(1)}[n] | \Phi_0[n] \rangle \right\}, \quad (10)$$

where

$$\begin{aligned} \hat{H}^{(1)}[n] &= \hat{V}_{ee} - \sum_{i=1}^N \{ u([n]; \mathbf{r}_i) + v_x([n]; \mathbf{r}_i) \} \\ &\equiv \hat{V}_{ee} - \sum_{i=1}^N v_{xu}([n]; \mathbf{r}_i), \end{aligned} \quad (11)$$

with $\Psi^{(1)}[n]$ being the first-order correction to the KS wavefunction $\Phi_0[n]$, due to perturbation $\hat{H}^{(1)}[n]$, and N being the number of particles in the system of interest. For brevity of notation, the following definition has been introduced

$$v_{xu}([n]; \mathbf{r}) = u([n]; \mathbf{r}) + v_x([n]; \mathbf{r}). \quad (12)$$

The second-order energy $E_c^{(2)}[n]$ is especially important because it is the initial slope in the adiabatic connection method for $E_c[n]$, even where $n(\mathbf{r})$ does not belong to a high-density system.

Very recently Ivanov, Burke and Levy (IBL) [27] have presented different forms of Eq. (10) particularly suitable for direct density variations. For any

two-electron diamagnetic density, they have derived an analytic expression for $v_c^{(2)}([n]; \mathbf{r})$, and arrived at the following closed-form expression connecting $E_c^{(2)}[n]$ and an integral of $v_c^{(2)}([n]; \mathbf{r})$, i.e.

$$E_c^{(2)}[n] = \frac{1}{2} \left\{ A[n] + \int v_c^{(2)}([n]; \mathbf{r}) n(\mathbf{r}) d\mathbf{r} \right\}, \quad (13)$$

where $A[n]$ is a functional of the density. For KS potentials for which all components vanish at infinity, Eq. (13) was first derived by Görling and Levy [23], and later expressed in a closed form by Ivanov et al. [28]. IBL have generalized formula (13) to any two-electron density regardless of the corresponding KS potential. The density functional $A[n]$ is identified [23,28] as

$$\begin{aligned} A[n] &= 2 \langle \varphi_0 | \frac{1}{2} u([n]; \mathbf{r}) | \varphi^{(1)} \rangle \\ &= \frac{1}{2} \int f(\mathbf{r}) n(\mathbf{r}) u([n]; \mathbf{r}) d\mathbf{r} \\ &\quad - \frac{1}{4} \int n(\mathbf{r}) u([n]; \mathbf{r}) d\mathbf{r} \int f(\mathbf{r}) n(\mathbf{r}) d\mathbf{r}, \end{aligned} \quad (14)$$

where φ_0 is the one-particle KS orbital, which is doubly occupied for a two-electron diamagnetic density, and $\varphi^{(1)}$ is the first-order correction to φ_0 due to the perturbation $\frac{1}{2} u([n]; \mathbf{r})$. The wavefunctions φ_0 and $\varphi^{(1)}$ can be expressed in terms of $n(\mathbf{r})$ by

$$\varphi_0 = \frac{1}{\sqrt{2}} n^{1/2}(\mathbf{r}), \quad (15)$$

and

$$\varphi^{(1)} = \left[f(\mathbf{r}) - \frac{1}{2} \int f(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} \right] \frac{n^{1/2}(\mathbf{r})}{\sqrt{2}}. \quad (16)$$

In Eqs. (14) and (16), $f(\mathbf{r})$ is a real one-body multiplicative operator which is the solution to

$$\begin{aligned} \nabla \cdot [n(\mathbf{r}) \nabla f(\mathbf{r})] \\ = n(\mathbf{r}) \left[u([n]; \mathbf{r}) - \frac{1}{2} \int n(\mathbf{r}) u([n]; \mathbf{r}) d\mathbf{r} \right]. \end{aligned} \quad (17)$$

When an appropriate transformation exists, such that the three-dimensional one-particle problem, Eq. (17), is reduced to three one-dimensional ones (i.e. the separation of variables is possible), then the analytic

solution to Eq. (17) exists, and can be obtained by two consecutive integrations over each of the coordinates.

By taking the functional derivative of $E_c^{(2)}[n]$ given by Eq. (13), we shall derive a new expression for $v_c^{(2)}([n]; \mathbf{r})$ for two-electron densities. In order to obtain an expression for $v_c^{(2)}([n]; \mathbf{r})$, we will make use of the following formula, which is simply a direct consequence of the definition of a functional derivative, i.e.

$$\left. \frac{\partial G[n + \varepsilon g]}{\partial \varepsilon} \right|_{\varepsilon=0} = \int \left. \frac{\delta G[\rho]}{\delta \rho(\mathbf{r})} \right|_{\rho=n} g(\mathbf{r}) d\mathbf{r}, \quad (18)$$

for all $g(\mathbf{r})$ such that $\int g(\mathbf{r}) d\mathbf{r} = 0$, keeping the particle number fixed through a small variation of the density. ($G[n]$ is an arbitrary functional of the density $n(\mathbf{r})$.) With this in mind, one obtains

$$\begin{aligned} & \int v_c^{(2)}([n]; \mathbf{r}) g(\mathbf{r}) d\mathbf{r} \\ &= \frac{1}{2} \left\{ \int a([n]; \mathbf{r}) g(\mathbf{r}) d\mathbf{r} \right. \\ & \quad + \int v_c^{(2)}([n]; \mathbf{r}) g(\mathbf{r}) d\mathbf{r} \\ & \quad \left. + \int f_c^{(2)}([n]; \mathbf{r}, \mathbf{r}') g(\mathbf{r}') n(\mathbf{r}) d\mathbf{r}' d\mathbf{r} \right\}. \quad (19) \end{aligned}$$

Here, $f_c^{(2)}([n]; \mathbf{r}, \mathbf{r}')$ is the static correlation kernel in the high-density scaling limit defined as

$$f_c^{(2)}([n]; \mathbf{r}, \mathbf{r}') = \frac{\delta v_c^{(2)}([n]; \mathbf{r})}{\delta n(\mathbf{r}')}, \quad (20)$$

and $a([n]; \mathbf{r})$ is the functional derivative of $A[n]$, namely

$$a([n]; \mathbf{r}) = \frac{\delta A[n]}{\delta n(\mathbf{r})}. \quad (21)$$

By noticing that Eq. (19) holds true for any $g(\mathbf{r})$ such that $\int g(\mathbf{r}) d\mathbf{r} = 0$, and some simple algebraic manipulations, we arrive at a new expression for $v_c^{(2)}([n]; \mathbf{r})$ in terms of $f_c^{(2)}([n]; \mathbf{r}, \mathbf{r}')$ and $a([n]; \mathbf{r})$, i.e.

$$\begin{aligned} v_c^{(2)}([n]; \mathbf{r}) &= \int f_c^{(2)}([n]; \mathbf{r}, \mathbf{r}') n(\mathbf{r}') d\mathbf{r}' \\ & \quad + a([n]; \mathbf{r}). \quad (22) \end{aligned}$$

In order to find the explicit form of $a([n]; \mathbf{r})$, we will use the approach introduced by IBL for taking the functional derivative of an energy functional given by a second-order expression. In turn, $A[n]$ is the second-order energy due to the perturbation $(\frac{1}{2})u([n]; \mathbf{r})$. Note that Eq. (14) is equivalent to

$$A[n] = 2 \langle \varphi^{(1)}[n] | \varepsilon_0[n] - \hat{h}_s[n] | \varphi^{(1)}[n] \rangle, \quad (23)$$

because the first-order wavefunction $\varphi^{(1)}[n]$ is the solution to

$$\begin{aligned} & \{ \varepsilon_0[n] - \hat{h}_s[n] \} \varphi^{(1)}[n] \\ &= \left\{ \frac{1}{2} u([n]; \mathbf{r}) \right. \\ & \quad \left. - \langle \varphi_0 | \frac{1}{2} u([n]; \mathbf{r}) | \varphi_0 \rangle \right\} \varphi_0[n]. \quad (24) \end{aligned}$$

In Eq. (23) and (24), all $n(\mathbf{r})$ -dependencies are shown explicitly and the one-particle KS Hamiltonian \hat{h}_s is given by

$$\hat{h}_s[n] = -\frac{1}{2} \nabla^2 + v_s([n]; \mathbf{r}). \quad (25)$$

The corresponding KS equations are

$$\hat{h}_s \varphi_k = \varepsilon_k \varphi_k, \quad \text{for } k = 0, 1, 2, \dots$$

$$\text{with } \varepsilon_0 < \varepsilon_1 \leq \varepsilon_2 \leq \dots \quad (26)$$

Following IBL and by making use of Eqs. (14), (23)–(26), we obtain an expression for the potential $a([n]; \mathbf{r})$,

$$\begin{aligned} a([n]; \mathbf{r}) &= 2 \int \frac{\varphi_0(\mathbf{r}') \varphi^{(1)}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \\ & \quad + \frac{1}{2} u([n]; \mathbf{r}) \frac{\varphi^{(1)}(\mathbf{r})}{\varphi_0(\mathbf{r})} \\ & \quad + \frac{1}{2} \left\{ \frac{\nabla^2 \xi(\mathbf{r})}{n(\mathbf{r})} - \frac{(\nabla \xi) \cdot (\nabla n)}{n^2(\mathbf{r})} \right. \\ & \quad \left. + \frac{\xi |\nabla n|^2}{n^3(\mathbf{r})} - \frac{\xi \nabla^2 n}{n^2(\mathbf{r})} \right\}, \quad (27a) \end{aligned}$$

Table 1

Comparison of the exact values for $E_c^{(2)}[n]$, $\int d\mathbf{r} v_c^{(2)}([n]; \mathbf{r})n(\mathbf{r})$, and $\iint f_c^{(2)}([n]; \mathbf{r}, \mathbf{r}')n(\mathbf{r}')n(\mathbf{r})d\mathbf{r}'d\mathbf{r}$, for density $n(\mathbf{r}) = (2a^3/\pi)e^{-2a\mathbf{r}}$, with those obtained from different approximations (a.u.)

	$E_c^{(2)}[n]$	$\int v_c^{(2)}([n]; \mathbf{r})n(\mathbf{r})d\mathbf{r}$	$\iint f_c^{(2)}([n]; \mathbf{r}, \mathbf{r}')n(\mathbf{r}')n(\mathbf{r})d\mathbf{r}'d\mathbf{r}$
Exact value	-0.0467	0.0177	0.3507
$E_c^{\text{LYP}}[n]$	-0.0567	-0.1093	-0.0175
$E_c^{\text{WV}}[n]$	-0.0480	-0.0734	-0.0298
$E_c^{\text{PBE}}[n]$	-0.0479	-0.0730	-0.0320

or in terms of $n(\mathbf{r})$ and $f(\mathbf{r})$,

$$a([n]; \mathbf{r}) = \int \frac{f(\mathbf{r}')n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \frac{1}{2}u([n]; \mathbf{r})f(\mathbf{r}) - \frac{3}{4}\int f(\mathbf{r})n(\mathbf{r})d\mathbf{r}u([n]; \mathbf{r}) + \frac{1}{2}\left\{ \frac{\nabla^2 \xi(\mathbf{r})}{n(\mathbf{r})} - \frac{(\nabla \xi) \cdot (\nabla n)}{n^2(\mathbf{r})} + \frac{\xi |\nabla n|^2}{n^3(\mathbf{r})} - \frac{\xi \nabla^2 n}{n^2(\mathbf{r})} \right\}, \quad (27b)$$

with

$$\xi(\mathbf{r}) = |\varphi^{(1)}|^2 = \frac{1}{2}\left[f(\mathbf{r}) - \frac{1}{2}\int f(\mathbf{r})n(\mathbf{r})d\mathbf{r} \right]^2 n(\mathbf{r}). \quad (28)$$

The combination of Eqs. (22), (27a), (27b) and (28) leads to a new point-wise formula for the high-density scaling limit of the correlation potential $v_c^{(2)}([n]; \mathbf{r})$ for a two-electron density in terms of an integral involving the static correlation kernel $f_c^{(2)}([n]; \mathbf{r}, \mathbf{r}')$.

Further, by multiplying both sides of Eq. (22) by $n(\mathbf{r})$ and integrating over all space, we obtain

$$\int v_c^{(2)}([n]; \mathbf{r})n(\mathbf{r})d\mathbf{r} - \iint f_c^{(2)}([n]; \mathbf{r}, \mathbf{r}')n(\mathbf{r}')n(\mathbf{r})d\mathbf{r}'d\mathbf{r} = 3A[n]. \quad (29)$$

We have made use of the fact that

$$\int a([n]; \mathbf{r})n(\mathbf{r})d\mathbf{r} = 3A[n], \quad (30)$$

because upon integrating by parts

$$\int n(\mathbf{r})\left\{ \frac{\nabla^2 \xi(\mathbf{r})}{n(\mathbf{r})} - \frac{(\nabla \xi) \cdot (\nabla n)}{n^2(\mathbf{r})} + \frac{\xi |\nabla n|^2}{n^3(\mathbf{r})} - \frac{\xi \nabla^2 n}{n^2(\mathbf{r})} \right\} d\mathbf{r} = 0. \quad (31)$$

Eqs. (22) and (29) can be readily manipulated to yield new easy-to-test constraints for $E_c^{(2)}[n]$ and integrals involving its functional derivatives, namely

$$6E_c^{(2)}[n] - 4\int v_c^{(2)}([n]; \mathbf{r})n(\mathbf{r})d\mathbf{r} + \iint f_c^{(2)}([n]; \mathbf{r}, \mathbf{r}')n(\mathbf{r}')n(\mathbf{r})d\mathbf{r}'d\mathbf{r} = 0, \quad (32a)$$

or

$$2E_c^{(2)}[n] - \iint f_c^{(2)}([n]; \mathbf{r}, \mathbf{r}')n(\mathbf{r}')n(\mathbf{r})d\mathbf{r}'d\mathbf{r} = 4A[n]. \quad (32b)$$

Condition (32a) is especially convenient for testing approximations to $E_c^{(2)}[n]$. However, it is a less stringent requirement than Eq. (32b) because of the possibility for an error cancellation between the integrals involving $v_c^{(2)}([n]; \mathbf{r})$ and $f_c^{(2)}([n]; \mathbf{r}, \mathbf{r}')$. In the above equations, $E_c^{(2)}[n]$ and $A[n]$ are identified as second-order energies and are always non-positive.

Last but not least, Eqs. (22), (29), (32a) and (32b) can undergo further density variations leading to new relationships among higher-order functional derivatives of $E_c^{(2)}[n]$ and $A[n]$. Examples include

$$\int \frac{\delta f_c^{(2)}([n]; \mathbf{r}, \mathbf{r}')}{\delta n(\mathbf{r}'')} n(\mathbf{r}'') d\mathbf{r}'' = - \frac{\delta a([n]; \mathbf{r})}{\delta n(\mathbf{r}')} \quad (33)$$

Table 2

Comparison of the exact values for $E_c^{(2)}[n]$, $\int v_c^{(2)}([n]; \mathbf{r})n(\mathbf{r})d\mathbf{r}$, and $\iint f_c^{(2)}([n]; \mathbf{r}, \mathbf{r}')n(\mathbf{r}')n(\mathbf{r})d\mathbf{r}'d\mathbf{r}$, for density $n(\mathbf{r}) = 2(2a/\pi)^{3/2} \times e^{-2ar^2}$, with those obtained from different approximations (a.u.)

	$E_c^{(2)}[n]$	$\int v_c^{(2)}([n]; \mathbf{r})n(\mathbf{r})d\mathbf{r}$	$\iint f_c^{(2)}([n]; \mathbf{r}, \mathbf{r}')n(\mathbf{r}')n(\mathbf{r})d\mathbf{r}'d\mathbf{r}$
Exact value	-0.0497	-0.0712	0.0134
$E_c^{\text{LYP}}[n]$	-0.0355	-0.1023	-0.0223
$E_c^{\text{WL}}[n]$	-0.0782	-0.1061	-0.0313
$E_c^{\text{PBE}}[n]$	-0.0813	-0.1096	-0.0332

stemming from Eq. (22), and from Eq. (29)

$$\int \int \frac{\delta f_c^{(2)}([n]; \mathbf{r}, \mathbf{r}')}{\delta n(\mathbf{r}'')} n(\mathbf{r}')n(\mathbf{r}'') d\mathbf{r}' d\mathbf{r}'' = -2a([n]; \mathbf{r}). \quad (34)$$

3. Numerical results

In this section, we shall present exact numbers for $\iint f_c^{(2)}([n]; \mathbf{r}, \mathbf{r}')n(\mathbf{r}')n(\mathbf{r})d\mathbf{r}'d\mathbf{r}$ for two different two-electron densities. The exact values are compared against the results from three different approximations to $E_c[n]$ which scale to a constant upon uniform scaling of the density for $\lambda \rightarrow \infty$. See Eq. (6). The first approximation we consider is the Lee–Yang–Parr (LYP) [29] functional, the second the Wilson–Levy (WL) [30] functional, and the third tested functional is the recently derived generalized-gradient approximation by Perdew, Burke, and Ernzerhof (PBE) [31,32].

The analytic forms of $f(\mathbf{r})$ for two model two-electron densities have been recently obtained, and the values of $A[n]$, $E_c^{(2)}[n]$ and $\int v_c^{(2)}([n]; \mathbf{r})n(\mathbf{r}')d\mathbf{r}$ have been calculated in Refs. [27] and [28]. By utilizing Eq. (29), we extract the exact numbers for $\iint f_c^{(2)}([n]; \mathbf{r}, \mathbf{r}')n(\mathbf{r}')n(\mathbf{r})d\mathbf{r}'d\mathbf{r}$ for the densities considered in Refs. [27] and [28]. (Equalities (32a) and (32b) might not be exactly satisfied because of round-off errors.)

In Table 1, we present the exact values for $E_c^{(2)}[n]$, $\int v_c^{(2)}([n]; \mathbf{r})n(\mathbf{r}')d\mathbf{r}$, and $\iint f_c^{(2)}([n]; \mathbf{r}, \mathbf{r}')n(\mathbf{r}')n(\mathbf{r}) \times d\mathbf{r}'d\mathbf{r}$, along with those obtained from LYP, WL and PBE functionals for density $n(\mathbf{r}) = (2a^3/\pi)e^{-2ar}$, $a > 0$. This density corresponds to KS potentials whose components vanish at infinity [28]. (The LYP results are calculated with the full

value of a given in Ref. [29], $a = 0.04918$, rather than rounded-off $a = 0.049$, which was used in Ref. [28].)

By making use of previous results by IBL, we calculate the exact value for $\iint f_c^{(2)}([n]; \mathbf{r}, \mathbf{r}')n(\mathbf{r}') \times n(\mathbf{r})d\mathbf{r}'d\mathbf{r}$ for $n(\mathbf{r}) = 2(2a/\pi)^{3/2}e^{-2ar^2}$, $a > 0$. This density is associated with a harmonic oscillator external potential which does not vanish as $\mathbf{r} \rightarrow \infty$ [27]. In Table 2, we make comparisons between the exact values and the results obtained by means of the tested approximations.

All tested approximations yield very good to reasonable results for $E_c^{(2)}[n]$ depending on the functional and the density. The results for $E_c^{(2)}[n]$ with $n(\mathbf{r}) = 2(2a/\pi)^{3/2}e^{-2ar^2}$, $a > 0$, are significantly worse than those with the hydrogen-like two-electron density, $n(\mathbf{r}) = (2a^3/\pi)e^{-2ar}$, $a > 0$. The three functionals produce poor results for $\int v_c^{(2)}([n]; \mathbf{r}) \times n(\mathbf{r}')d\mathbf{r}$ and especially for $\iint f_c^{(2)}([n]; \mathbf{r}, \mathbf{r}') \times n(\mathbf{r}')n(\mathbf{r})d\mathbf{r}'d\mathbf{r}$. They cannot capture the positive sign of the integral involving the high-density limit of the static correlation kernel. This is not surprising since none of them has been designed with constraints on the functional derivatives in mind. Yet it is exactly such formal conditions that are essential for constructing new approximations leading to accurate results from time-dependent KS calculations.

4. Closing remarks

In order to arrive at new correlation energy functionals with improved functional derivatives, a knowledge of the exact properties of the correlation potential $v_c([n]; \mathbf{r})$ and the static correlation kernel $f_c([n]; \mathbf{r}, \mathbf{r}')$, is needed. With this in mind, we have derived a new expression for $v_c([n]; \mathbf{r})$ in the high-

density scaling limit for two-electron densities. This scaling limit is of a special interest because it is the second-order contribution to $E_c[n]$ for any density $n(\mathbf{r})$ of chemical interest. The new analytic formula for $v_c^{(2)}([n]; \mathbf{r})$ for two-electron diamagnetic densities features an explicitly known component and integral involving $f_c^{(2)}([n]; \mathbf{r}, \mathbf{r}')$. As a direct consequence of our results for $v_c^{(2)}([n]; \mathbf{r})$, we have obtained a closed-form expression for the difference $\int v_c^{(2)}([n]; \mathbf{r}) n(\mathbf{r}') d\mathbf{r} - \int \int f_c^{(2)}([n]; \mathbf{r}, \mathbf{r}') n(\mathbf{r}') n(\mathbf{r}) d\mathbf{r}' d\mathbf{r}$ for two-electron densities. By using previous results for the exact values of $\int v_c^{(2)}([n]; \mathbf{r}) n(\mathbf{r}') d\mathbf{r}$ for two model two-electron densities, we have calculated the exact values corresponding to $\int \int f_c^{(2)}([n]; \mathbf{r}, \mathbf{r}') n(\mathbf{r}') n(\mathbf{r}) d\mathbf{r}' d\mathbf{r}$ for those model densities. The exact numbers have been compared to results from three different approximations to $E_c[n]$. None of the considered functionals yields the correct positive sign of $\int \int f_c^{(2)}([n]; \mathbf{r}, \mathbf{r}') n(\mathbf{r}') n(\mathbf{r}) d\mathbf{r}' d\mathbf{r}$ for the test densities.

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