Exact non-additive kinetic potentials in realistic chemical systems

DE SILVA, Piotr, WESOLOWSKI, Tomasz Adam

Abstract
In methods based on frozen-density embedding theory or subsystem formulation of density functional theory, the non-additive kinetic potential (vtnad(r)) needs to be approximated. Since vtnad(r) is defined as a bifunctional, the common strategies rely on approximating vtnad[ρA,ρB](r). In this work, the exact potentials (not bifunctionals) are constructed for chemically relevant pairs of electron densities (ρA and ρB) representing: dissociating molecules, two parts of a molecule linked by a covalent bond, or valence and core electrons. The method used is applicable only for particular case, where ρA is a one-electron or spin-compensated two-electron density, for which the analytic relation between the density and potential exists. The sum ρA + ρB is, however, not limited to such restrictions. Kohn-Sham molecular densities are used for this purpose. The constructed potentials are analyzed to identify the properties which must be taken into account when constructing approximations to the corresponding bifunctional. It is comprehensively shown that the full von Weizsäcker component is indispensable in order to […]

Reference
DE SILVA, Piotr, WESOLOWSKI, Tomasz Adam. Exact non-additive kinetic potentials in realistic chemical systems. Journal of Chemical Physics, 2012, vol. 137, no. 9, p. 094110

DOI : 10.1063/1.4749573

Available at:
http://archive-ouverte.unige.ch/unige:22918

Disclaimer: layout of this document may differ from the published version.
Exact non-additive kinetic potentials in realistic chemical systems

Piotr de Silva and Tomasz A. Wesolowski

1 Université de Genève, Département de Chimie Physique 30, quai Ernest-Ansermet, CH-1211 Genève 4, Switzerland
2 K. Gumiński Department of Theoretical Chemistry Faculty of Chemistry, Jagiellonian University, R. Ingardena 3, 30-060 Kraków, Poland

(Received 22 June 2012; accepted 19 August 2012; published online 7 September 2012)

In methods based on frozen-density embedding theory or subsystem formulation of density functional theory (subsystem DFT), the non-additive kinetic potential ($v_{\text{nad}}^\text{ad}(r)$) needs to be approximated. Since $v_{\text{nad}}^\text{ad}(r)$ is defined as a bifunctional, the common strategies rely on approximating $v_{\text{nad}}^\text{ad}(\rho_A, \rho_B)(r)$. In this work, the exact potentials (not bifunctionals) are constructed for chemically relevant pairs of electron densities ($\rho_A$ and $\rho_B$) representing: dissociating molecules, two parts of a molecule linked by a covalent bond, or valence and core electrons. The method used is applicable only for particular case, where $\rho_A$ is a one-electron or spin-compensated two-electron density, for which the analytic relation between the density and potential exists. The sum $\rho_A + \rho_B$ is, however, not limited to such restrictions. Kohn-Sham molecular densities are used for this purpose. The constructed potentials are analyzed to identify the properties which must be taken into account when constructing approximations to the corresponding bifunctional. It is comprehensively shown that the full von Weizsäcker component is indispensable in order to approximate adequately the non-additive kinetic potential for such pairs of densities. © 2012 American Institute of Physics.

I. INTRODUCTION

In numerical simulations based on frozen-density embedding theory (FDET) or subsystem formulation of density functional theory (subsystem DFT), the non-additive kinetic potential ($v_{\text{nad}}^\text{ad}(r)$) needs to be approximated. The potential $v_{\text{nad}}^\text{ad}(r)$ is uniquely defined by the pair of electron densities $\rho_A$ and $\rho_B$ at which it is evaluated. We will refer to this correspondence as bifunctional and denote it with $v_{\text{nad}}^\text{ad}(\rho_A, \rho_B)(r)$, which is defined as:

$$v_{\text{nad}}^\text{ad}(\rho_A, \rho_B)(r) = \frac{\delta T_{\text{nad}}^\text{ad}(\rho_A, \rho_B)}{\delta \rho(r)}|_{\rho=\rho_A},$$

where $T_{\text{nad}}^\text{ad}(\rho_A, \rho_B)$ denotes the bifunctional of non-additive kinetic energy, which in turn is defined in the constrained search procedure:

$$T_{\text{nad}}^\text{ad}(\rho_A, \rho_B) = \min_{\Psi_{\text{f}}} \left\{ \langle \Psi_{\text{f}} | -\frac{1}{2} \nabla^2 + v_{\text{nad}}^\text{ad}(\rho_A, \rho_B) | \Psi_{\text{f}} \rangle \right\},$$

where $\Psi_{\text{f}}$ denotes a trial many-electron wave function of single-determinant form. The above mentioned formal frameworks attract increasing interests and a multitude of computational methods have been developed. Multilevel type of numerical simulations based on FDET, in which a part of the system (environment) is treated in a simplified manner, are quite abundant in the literature. Besides technical details, the developed methods, differ in the way the electron density of the environment is generated and in the targeted properties. A representative applications targeting such properties as the energy differences, hyperfine structure, circular dichroism, electronic excitations, NMR chemical shifts, ligand-field splittings of f levels in rare earth elements, etc., can be found in Refs. 9–18. As far as fully variational methods based on subsystem DFT are concerned, they are used to study mainly intermolecular interactions.9,19–23 In all these methods the non-additive kinetic potential is approximated as a bifunctional. If the total-energy or energy differences are to be evaluated consistently with the density, also the bifunctional for the non-additive kinetic energy which is consistent with the corresponding potential (its functional derivative) needs also to be approximated.

It is worthwhile to point out closely related methods also hinging on approximations to the bifunctional for the non-additive kinetic potential (and/or energy): (i) the method to study couplings between excitations in similar chromophore introduced by Neugebauer24 which is based on generalization of subsystem DFT to excited states,25 (ii) the method introduced by Carter26 and co-workers and followed by others27 in which the potential derived in FDET for embedding a reference system of non-interacting electrons (Eq. (3) in Ref. 28 was used for embedding an interacting system, the formal justification of such a combination was given only recently),3 and (iii) the method to embed systems described at the generalized Kohn-Sham (KS) level, i.e., using hybrid exchange-correlation functionals and non-local effective potentials.29

Besides FDET and subsystem DFT, $v_{\text{nad}}^\text{ad}(r)$ features also in recently developed partition DFT framework. Each of these formalisms formulates a different mathematical problem, involves different exact relations, and if converted to a computational methods, hinges on approximations for different quantities. In the case of subsystem DFT, the integer occupancies of each subsystem are considered as input quantities and the relevant equations in the exact limit lead to the
ground-state energy of the whole system. Such problem has infinite number of solutions in the exact functional limit because there is an infinite number of ways the total ground state density can be partitioned and the Hohenberg-Kohn density functional depends only on the total density. In the case of partition DFT, the ground-state density is also reached in the exact functional limit but additionally the partitioning is unique although might involve non-integer number of electrons in each subsystem. The unique partitioning is achieved due to an additional condition of minimizing the reference energy. In the case of frozen-density embedding theory, however, the relevant equations do not target the ground-state energy of the whole system but the upper bound of the total energy which might be higher than the ground-state energy due to additional constraints not present in the other two formal frameworks (the total density must not be smaller than a given a priori frozen density).

Whereas each of the three formal frameworks involves \( v_{\text{F}}^\text{rad}(\mathbf{r}) \), the evaluation of this potential follows different strategies. Partition DFT does not hinge on any approximation to the bifunctional \( v_{\text{F}}^\text{rad}(\rho_A, \rho_B)(\mathbf{r}) \). \( v_{\text{F}}^\text{rad}(\mathbf{r}) \) is just one component of the partitioning potential, which is constructed in the course of calculations leading to unique partitioning of the initially known total electron density. The computational methods based on partition DFT in which, instead of constructing the partition potential explicitly, its non-additive kinetic component would be approximated by means of an explicit bifunctional has not been developed so far. Such methods would be naturally seen as extensions of subsystem DFT and FDET to non-integer occupancies. In both subsystem DFT and FDET, the conventional strategy hinges on approximations to the bifunctional \( v_{\text{F}}^\text{rad}(\rho_A, \rho_B)(\mathbf{r}) \) and the knowledge of its exact properties is crucial for both the development of adequate approximations and for establishment of the criteria for their applicability. For instance, approximating \( v_{\text{F}}^\text{rad}(\rho_A, \rho_B)(\mathbf{r}) \) by means of deriving it from the gradient-expansion or generalized-gradient expansion approximations to the kinetic energy functional \( \tilde{T}^\text{GGA}[\rho] \),

\[
\begin{align*}
\tilde{T}^\text{GGA}[\rho] & = \frac{\delta T^\text{GGA}[\rho]}{\delta \rho} \bigg|_{\rho=\rho_A+\rho_B} - \frac{\delta T^\text{GGA}[\rho]}{\delta \rho} \bigg|_{\rho=\rho_A} \\
& = \frac{\delta T^\text{GGA}[\rho]}{\delta \rho} \bigg|_{\rho=\rho_A+\rho_B} - \frac{\delta T^\text{GGA}[\rho]}{\delta \rho} \bigg|_{\rho=\rho_A}
\end{align*}
\]

leads to the potential which is known to fail if the overlap between \( \rho_A \) and \( \rho_B \) is large.\(^{31-33} \) This leaves the case where the subsystems are linked by covalent bonds rather outside of the domain of applicability of such approximations.\(^{23,34} \) On the other hand, violation of the exact limit at \( \rho_A(\mathbf{r}) \rightarrow 0 \) for such \( \rho_B \) that \( \int \rho_B(\mathbf{r})d\mathbf{r} = 2 \) by the potentials given in Eq. (3) leads to the artificial potential well near the nuclei in the environment.\(^{35} \)

Recently, an alternative strategy to generate the potential \( v_{\text{F}}^\text{rad}(\mathbf{r}) \) which circumvents the problem of approximating the bifunctional by means to explicit construction of \( v_{\text{F}}^\text{rad}(\mathbf{r}) \) using the numerical inversion procedures\(^{36,37} \) has been proposed.\(^{38-41} \) Knowing exact potential \( v_{\text{F}}^\text{rad}(\mathbf{r}) \) for a given specific pair \( \rho_A \) and \( \rho_B \) even without knowing the corresponding bifunctional \( v_{\text{F}}^\text{rad}(\rho_A, \rho_B)(\mathbf{r}) \) is very desirable from methodological point of view as a reference for developing approximations to \( v_{\text{F}}^\text{rad}(\rho_A, \rho_B)(\mathbf{r}) \). In principle, methods based on numerical inversion should yield the exact potential \( v_{\text{F}}^\text{rad}(\mathbf{r}) \) for the chosen pair \( \rho_A \) and \( \rho_B \). In practice, the inverted potentials do not correspond exactly to the densities. In the recent work by Fux et al.,\(^{41} \) where this correspondence was studied in detail, the difference between the target density and the density obtained using the inverted potential could not be made arbitrarily small. We note that, in the case of analytically solvable systems,\(^{42,43} \) these two densities agree with arbitrary accuracy. For this reason, we investigate here the reference potentials \( v_{\text{F}}^\text{rad}(\rho_A, \rho_B)(\mathbf{r}) \) which are also obtained by means of analytic inversion.

Some of the objectives of the present work are similar to these in previously published work by Savin and Wesolowski,\(^{42} \) which deals with a fictitious, non-interacting spherically symmetric system. The crucial differences are the following: (i) the discussion is extended to chemically relevant systems, such as atoms, di- and tri-atomics, with realistic Kohn-Sham potentials, (ii) the partitioning of the electron density goes beyond a simple core-valence separation and represents subsystems which are covalently or non-covalently bound and at equilibrium or dissociation, (iii) the numerical procedure used in the present work takes into account recently reported findings concerning the interpretation of the Kohn-Sham potential if finite basis sets are used,\(^{43} \) (iv) the performance of fundamental approximations for the non-additive kinetic energy functional is discussed, (v) the origin and role of barriers and value shifts in \( v_{\text{F}}^\text{rad}(\mathbf{r}) \) is analyzed in more detail. The main objective of the present work is providing the reference quantities rather than proposing any particular strategy for approximating \( v_{\text{F}}^\text{rad}(\rho_A, \rho_B)(\mathbf{r}) \) in large-scale numerical simulations based on either subsystem DFT or FDET. For these reasons the smallest molecules allowing for studies of such model cases were chosen. We stress that the method used to obtain the exact potential \( v_{\text{F}}^\text{rad}(\mathbf{r}) \) is not intended to be an alternative for conventional approaches in practical numerical simulations. It is applicable only for particular case, where \( \rho_A \) is a one-electron or spin-compensated two-electron density. The analytic relation between the density and potential exists only for one-electron systems or spin-compensated two-electron systems considered in this work.

II. RECONSTRUCTION OF \( v_{\text{F}}^\text{rad}(\mathbf{r}) \)

In DFT the ground-state density \( \rho_0(\mathbf{r}) \) is the solution of the Euler-Lagrange equation

\[
\mu = \frac{\delta E_{\text{F}}[\rho]}{\delta \rho(\mathbf{r})} \bigg|_{\rho=\rho_0} = \frac{\delta T[\rho]}{\delta \rho(\mathbf{r})} \bigg|_{\rho=\rho_0} + v_1[\rho_0](\mathbf{r}),
\]

where \( E_{\text{F}}[\rho] \) is the total energy functional, \( T[\rho] \) non-interacting kinetic energy functional, \( v_1[\rho_0](\mathbf{r}) \) is the Kohn-Sham potential and \( \mu \) is the chemical potential. From Eq. (4) it is evident that at the solution point the kinetic potential is equal to the negative Kohn-Sham potential shifted by a constant,

\[
v_1[\rho_0](\mathbf{r}) = \frac{\delta T[\rho]}{\delta \rho(\mathbf{r})} \bigg|_{\rho=\rho_0} = -v_0[\rho_0](\mathbf{r}) + \mu.
\]
In FDET the non-additive kinetic potential bifunctional is defined as a difference of kinetic potentials evaluated at two densities
\[
v_{i}^{\text{nad}}(\rho_A, \rho_B) = \frac{\delta T_i[\rho]}{\delta \rho(\mathbf{r})} \bigg|_{\rho=\rho_A+\rho_B} - \frac{\delta T_i[\rho]}{\delta \rho(\mathbf{r})} \bigg|_{\rho=\rho_A} . \quad (6)
\]
When \(\rho_B\) is a fixed density, \(\rho_A\) is the minimizer of the total energy bifunctional \(E_i[\rho_A, \rho_B]\) and \(\rho_A + \rho_B\) is the minimizer of the total energy functional \(E_i[\rho]\), then inserting Eq. (5) into Eq. (6) gives the following formula:
\[
v_{i}^{\text{nad}}(\rho_A, \rho_B) = v_i[\rho]_{\rho=\rho_A} - v_i[\rho]_{\rho=\rho_A+\rho_B} . \quad (7)
\]
Thus, in order to obtain the exact non-additive kinetic potential for a pair of densities, one has to subtract two Kohn-Sham potentials, in which these densities are ground-state densities.

In the Kohn-Sham method, the KS equations
\[
\left[-\frac{1}{2} \nabla^2 + v_i[\rho](\mathbf{r})\right] \phi_i = \epsilon_i \phi_i \quad (8)
\]
are solved iteratively yielding the self-consistent density \(\rho_0(\mathbf{r})\) and potential \(v_i(\mathbf{r})\) at the end of the procedure. The KS potential is a result of inserting the converged density into the approximate formula used in calculations
\[
v_i(\mathbf{r}) = \frac{N_{\text{nuc}}}{2} - \frac{Z_i}{|\mathbf{r} - \mathbf{R}_i|} + \int \frac{\rho(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{xc}[\rho](\mathbf{r}). \quad (9)
\]
The total density can be decomposed into an arbitrary sum of two densities \(\rho_0 = \rho_A + \rho_B\). To calculate \(v_{i}^{\text{nad}}(\rho_A, \rho_B)\) with Eq. (7) one has to have the Kohn-Sham potential for \(\rho_A\) available. There is a number of methods proposed in literature to obtain the Kohn-Sham potential for arbitrary densities by means of numerical inversion. In this paper we obtain the exact Kohn-Sham potentials analytically by restricting \(\rho_A\) only to the class of spin-compensated two-electron densities. For such densities the Kohn-Sham equation (Eq. (8)) can be inverted directly, and the potential \(v_i[\rho_A](\mathbf{r})\) reads thus,
\[
v_i[\rho_A](\mathbf{r}) = \frac{1}{2} \nabla^2 \sqrt{\rho_A(\mathbf{r})} + \text{constant} = \frac{1}{2} \nabla^2 \sqrt{\rho_A(\mathbf{r})} + \frac{1}{8} \frac{|\nabla \rho_A(\mathbf{r})|^2}{\rho_A(\mathbf{r})} + \text{constant}, \quad (10)
\]
where constant is chosen in such a way that \(\lim_{\mathbf{r} \to \infty} v_i[\rho_A](\mathbf{r}) = 0\).

According to the presented scheme any partitioning of \(\rho\) into two densities \(\rho_A\) and \(\rho_B\), where \(\rho_A\) is a spin-compensated, two-electron density, would enable to calculate the corresponding non-additive kinetic potential. Here, we take an advantage of the fact, that the total density comes from Kohn-Sham calculations and Kohn-Sham orbitals are available as well. This allows for a convenient parameterization of \(\rho_A\) and \(\rho_B\), which enables to control and adjust the character of these densities from the point of view of the electronic structure of the whole system. Namely, the densities are constructed as linear combinations of orbital densities
\[
\rho_A(\mathbf{r}) = \sum_{i=1}^{N} 2\alpha_i |\phi_i(\mathbf{r})|^2, \quad \rho_B(\mathbf{r}) = \sum_{i=1}^{N} (2 - \alpha_i) |\phi_i(\mathbf{r})|^2, \quad (11)
\]
where \(N\) is the number of double occupied KS orbitals.

Summarizing, the procedure of constructing the exact reference potentials \(v_i^{\text{nad}}(\mathbf{r})\) takes the following steps:

- Do Kohn-Sham calculations for a chosen system (with any approximate, multiplicative exchange-correlation functional) and obtain: the ground-state density \(\rho_0(\mathbf{r})\), KS orbitals \(|\phi_i(\mathbf{r})\rangle\) and KS potential \(v_i[\rho_0(\mathbf{r})]\) (Eq. (9)).
- Choose the coefficients \(\alpha_i\) in Eq. (11) to define the frozen density \(\rho_B(\mathbf{r})\) and the target density \(\rho_A(\mathbf{r})\).
- Insert \(\rho_A(\mathbf{r})\) into Eq. (10) to obtain \(v_i[\rho_A(\mathbf{r})]\).
- Insert \(v_i[\rho_A(\mathbf{r})]\) and \(v_i[\rho_0(\mathbf{r})]\) into Eq. (7) to obtain \(v_i^{\text{nad}}(\rho_A, \rho_B)(\mathbf{r})\).

This scheme gives the exact non-additive kinetic potential only if the orbitals used are the exact solutions of the Kohn-Sham equations with a given approximated Kohn-Sham potential. In practical calculations the linear combination of atomic orbitals (LCAO) approximation is usually employed and the differential equation is replaced by a generalized matrix eigenvalue problem. As a consequence of the basis set incompleteness, the exact Kohn-Sham potential for the obtained approximate ground-state density \(\rho^{\text{LCAO}}_0(\mathbf{r})\) is not equal to the potential in Eq. (9)
\[
v_i[\rho^{\text{LCAO}}_0(\mathbf{r})] \neq \sum_{i=1}^{N_{\text{nuc}}} \frac{Z_i}{|\mathbf{r} - \mathbf{R}_i|} + \int \frac{\rho^{\text{LCAO}}_0(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{xc}[\rho^{\text{LCAO}}_0(\mathbf{r})]. \quad (12)
\]
For a more detailed analysis of this inequality and further consequences, the reader is referred to Ref. 43. What is relevant to the present analysis is that the discrepancies between potentials in Eq. (12) can be locally diminished by enlarging the basis set. However, even in the most expanded basis sets available, one can expect qualitative failures in some regions of space. This will certainly be the case at nuclei, where the density exhibits a cusp. The exact density fulfils the Kato cusp condition, whereas for LCAO approximation, the behaviour of the density at positions of nuclei is determined by available basis functions. Also far from the molecule, where \(\rho^{\text{LCAO}}_0\) is negligible, the behaviour of the density is unphysical and dictated by the slowest decaying basis function. The same situation applies to the asymptotic region of the target density \(\rho_A(\mathbf{r})\). Finally, problems may occur at nodal surfaces of orbitals with the dominant share in \(\rho_A(\mathbf{r})\). This means that
much caution is needed while interpreting the reference potentials obtained from the outlined procedure.

III. RESULTS

Before discussing the numerical results obtained for non-integer values of the parameter $a_1$, we summarize the key features of the exact non-additive kinetic potential for $\rho_A$ and $\rho_B$ corresponding to $a_1 = 1$ in Eq. (11) (for a full discussion, see Ref. 42). If $a_1 = 1$, $\rho_A$ is equal to the lowest-lying Kohn-Sham orbital density for the whole system ($\rho_A = 2\phi_{max}^2$). In this case, the embedded orbital, i.e., the ground-state wave function yielding $\rho_A$, is just $\phi_A = \sqrt{\frac{\rho_A}{2}} = \phi_1$. We use the fact, that the lowest lying Kohn-Sham orbital of any system is nodeless.46 resulting in the equality: $\phi_1 = |\phi_1|$. The two densities $\rho_A$ and $\rho_A + \rho_B$ are thus the ground-state densities for two non-interacting electron systems differing in the number of electrons but sharing the same effective potential which is equal to $v_1[\rho_A + \rho_B]$. As a consequence $v_1^{\text{nad}}[\rho_A, \rho_B](\mathbf{r}) = 0$. Nothing has to be added to the Kohn-Sham potential for the whole system $v_1[\rho_A + \rho_B]$ to obtain $\rho_A$ as the ground-state density of a spin-compensated two-electron system.

The situation is quite different if $a_1 = 1$ and $i \geq 2$. Although, as in the previously discussed case $\rho_A = 2\phi_{max}^2$ but $\phi_A \neq \phi_1$. If $\phi_1$ is one of the higher lying orbitals, it must contain nodes (to assure orthogonality to $\phi_1$). As a result, $\phi_A = \sqrt{\frac{\rho_A}{2}} = |\phi_i| \neq \phi_i$. Although $\phi_1$ is an eigenfunction of the effective Kohn-Sham operator, it is not an orbital of the ground state of a two-electron system in the potential $v_1[\rho_A + \rho_B]$ but one of its excited states. To get the modulus of an orbital as the ground state, one has to add Dirac delta barriers in the positions of nodes.47 This means that in this case $v_i^{\text{nad}}[\rho_A, \rho_B](\mathbf{r}) = 0$ everywhere except for the nodal surfaces, where it becomes a delta function. The studies of $v_i^{\text{nad}}[\rho_A, \rho_B](\mathbf{r})$ in analytically solvable systems confirm, indeed, such behaviour of the non-additive kinetic potential if the target density approaches orbital density of the other than lowest Kohn-Sham orbital.

Turning back to fractional values of $a_i$, the total densities in the considered systems were obtained by solving the Kohn-Sham equations applying the LCAO approximation using Slater type of orbitals (STO) and the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional implemented in the ADF program.49 As noticed in Sec. II, the key numerical difficulty in obtaining $v_i^{\text{nad}}[\rho_A, \rho_B](\mathbf{r})$ as the difference between the two potentials ($v_i[\rho_A](\mathbf{r}) - v_i[\rho_A + \rho_B](\mathbf{r})$) is the availability of the exact Kohn-Sham potential $v_i[\rho_A + \rho_B](\mathbf{r})$, whereas the potential $v_i[\rho_A](\mathbf{r})$ is given analytically. In the case of LCAO calculations leading to some ground state density $\rho_0^{\text{LCAO}}$, the potential $v_i[\rho_0^{\text{LCAO}}](\mathbf{r})$ is not available but only the Kohn-Sham potential given in Eq. (9). The use of an extensive basis set is crucial to minimize the discrepancy between the exact Kohn-Sham potential $v_i[\rho_0^{\text{LCAO}}](\mathbf{r})$ and the potential available in practice (Eq. (9)). To this end, a QZ4P basis set was used in all calculations. Additionally, the self-consistent procedure (SCF) convergence criterion was set to a stringent value $10^{-10}$ and an extensive integration grid was used (INTEGRATION = 12).

The reference non-additive kinetic potentials were calculated by following the procedure outlined in Sec. II. Due to the unphysical asymptotic behavior of LCAO densities, the condition that $\lim_{r \to \infty} v_i[\rho_A](\mathbf{r}) = 0$ is not really desirable in this case. Instead, the constant in Eq. (10) is set to the largest of eigenvalues corresponding to Kohn-Sham orbitals that form $\rho_A$ (Eq. (11)). The potentials are shown in all figures only for the ranges, where the reconstruction procedure is reliable, i.e., where the differences between $v_i[\rho_0^{\text{LCAO}}](\mathbf{r})$ and the potential available in practice (Eq. (9)) are insignificant.

In addition to reference potentials, its approximate counterparts were calculated using two known approximate kinetic energy functionals, that are exact for some limiting cases. The Thomas-Fermi (TF) functional is exact for the homogeneous electron gas and for an atom with infinite nuclear charge.50 It is the common starting point for the generalized gradient approximation (GGA) kinetic energy functionals31 which obey the uniform electron gas limit by construction. Applying TF approximation to calculate the non-additive kinetic potential gives the following formula:

$$v_i^{\text{nad(TF)}}[\rho_A, \rho_B](\mathbf{r}) = \frac{5}{3} C_{TF} \left( (\rho_A + \rho_B)^{2/3} - \rho_A^{2/3} \right),$$

where $C_{TF} = \frac{3}{m} (3\pi^2)^{2/3}$.

The potential derived from Eq. (13), when applied to molecular systems, has cusps at nuclei and decays exponentially in the asymptotic region. These are known flaws of this approximation, as the exact potential should behave as $\sim \frac{1}{r}$. This proper behaviour is recovered by the von Weizsäcker (W) approximation, which is exact for one or two spin-compensated electrons. Employing this approximation as a starting point in the development of some kinetic energy functionals is proposed by an alternative strategy to approximate the kinetic energy functional.32,33 The non-additive kinetic potential derived from W approximation takes the form

$$v_i^{\text{nad(W)}}[\rho_A, \rho_B](\mathbf{r}) = \frac{1}{8} \left( \frac{(\nabla \rho_A + \rho_B)^2}{(\rho_A + \rho_B)^2} - \frac{|\nabla \rho_A|^2}{\rho_A^2} \right) - \frac{1}{4} \left( \frac{\nabla^2 \rho_A + \rho_B}{(\rho_A + \rho_B)} - \frac{\nabla^2 \rho_A}{\rho_A} \right).$$

Although this approximation is expected to be very good near the nuclei and far from the molecule, it misses completely the Pauli potential which is responsible for the Pauli repulsion effect. A severe consequence of this is that the W approximation for $v_i^{\text{nad}}[\rho_A, \rho_B](\mathbf{r})$ fails completely whenever $\rho_A$ is proportional to the total density. If $\rho_A = \lambda (\rho_A + \rho_B)$, then $v_i^{\text{nad(W)}}[\rho_A, \rho_B](\mathbf{r})$ vanishes everywhere in the physical space.

The outlined procedure is applicable to both closed- and open-shell molecular systems. The only constraint is that $\rho_A$ has to be a one-electron or spin-compensated two-electron density. The present work is focused on identifying and investigating the qualitative features of $v_i^{\text{nad}}[\rho_A, \rho_B](\mathbf{r})$, which do not depend on multiplicity of neither $\rho = \rho_A + \rho_B$ nor $\rho_A$. For this reason, the reference potentials discussed in this section were constructed for the closed-shell case in selected representative systems.
A. Beryllium atom

Savin and Wesolowski\textsuperscript{42} analyzed the exact non-additive kinetic potential for a fictitious spherically symmetric system of four non-interacting electrons in $-\frac{1}{r}$ Kohn-Sham potential. Although this potential cannot be treated as a reasonable approximation for any realistic system, the analogy with the beryllium atom is straightforward. Here we examine this analogy further by reconstructing $v_{\text{rad}}^\text{rad}(r)$ from KS orbitals obtained from standard DFT calculations with approximate, but more realistic potential. Opposite to the potential $-\frac{1}{r}$ analyzed in Ref. 42 which is equal to the exact Kohn-Sham potential for beryllium only at the long range limit, the potential used in this work comprises exact expression for the coulomb part of the Kohn-Sham potential and an approximated (PBE) expression for its exchange-correlation part. The beryllium atom possesses four electrons, which occupy two orbitals $\phi_1$ and $\phi_2$. The calculated orbital energies are $\varepsilon_{1s} = -3.90$ a.u. and $\varepsilon_{2s} = -0.21$ a.u. In this case, the partitioning of the density according to Eq. (11) is determined by just one parameter $\alpha \in [0, 1]$: 

$$\rho_A = 2(\alpha \phi_1^2 + (1 - \alpha)\phi_2^2),$$
$$\rho_B = 2((1 - \alpha)\phi_1^2 + \alpha\phi_2^2).$$

Figure 1(a) shows the non-additive kinetic potential for the frozen density taken as essentially the valence density with a small admixture of core density ($\alpha = 0.99$). The potential consists of two plateaus with a smooth transition between them occurring approximately at 1 Å. The value of the shift between these plateaus is equal to $\Delta \varepsilon = \varepsilon_{2s} - \varepsilon_{1s}$. Decreasing the mixing parameter to $\alpha = 0.9$ (Fig. 1(b)) makes the transition region move closer to the nucleus. Additionally a bump between the shifted and transition regions in the potential starts to be visible. This trend is continued further with the decrease of $\alpha$ (Figs. 1(c)–1(h)). The bump transforms into another of a position, which grows, get narrower and moves toward the position of a node in $\phi_{2s}$ at 0.31 Å, while the shifted plateau disappears. In the limit $\alpha \rightarrow 0^+$ the non-additive kinetic potential converges to a delta function centered at the node of $\phi_2$. These results fully agree with the results obtained by Savin and Wesolowski for the fictitious four-electron atom. The non-additive kinetic potentials for both cases have exactly the same features.

In addition to the exact reference potentials, Fig. 1 shows also the approximated counterparts calculated from two fundamental approximations to the kinetic energy functional, namely Thomas-Fermi (dotted lines) and von Weizsäcker (dashed lines) approximations. The comparison of plots shows that the potentials obtained from the TF approximation do not resemble even qualitatively the exact non-additive kinetic potentials. This approximation is not able to reproduce any of the key features of the exact potential, that is the shift in the values and the barrier. Instead, it exhibits a spurious cusp at the nucleus. On the other hand, the W approximation seems to be resonable at least in some regions of space and for some choices of the mixing parameter $\alpha$. For $\alpha = 0.99$, the W potential agrees very well with the exact $v_{\text{rad}}^\text{rad}(r)$ in the transition and the outer region. However, in the inner regions it fails completely as it produces a well instead of a shifted plateau. When $\alpha$ decreases the well and the barrier in the W potential flatten (Figs. 1(b) and 1(c)) and finally the whole potential disappears if $\alpha = 0.5$ (Fig. 1(d)). Decreasing further the value of the mixing parameter makes the W potential to reveal its barrier and well structure (Figs. 1(e) and 1(f)). Again, the position of the barrier coincides with the barrier in the exact potential, however it lacks the value shift in the inner region. The well remains a spurious feature. When $\rho_A$ is mostly the valence electron density, the W potential reproduces the barrier almost perfectly (Figs. 1(g) and 1(h)). Unfortunately, the barrier is surrounded from both sides by wells, which are not present in the exact potential.

B. He-Li\textsuperscript{+}

The system consisting of the helium atom and the lithium cation is used as a model representing two non-covalently bonded subsystems. It comprises four electrons occupying two Kohn-Sham orbitals. The optimized equilibrium distance between the nuclei is 1.89 Å. The lowest-lying orbital $\phi_1$ is localized mostly on lithium and its energy is $\varepsilon_{1s} = -2.21$ a.u. The second orbital $\phi_2$ with the corresponding eigenvalue $\varepsilon_{2s} = -0.86$ a.u. is centered mostly on helium. Analogously as for the beryllium, the choice of the density pairs is controlled by the mixing parameter $\alpha \in [0, 1]$: 

$$\rho_A = 2(\alpha \phi_1^2 + (1 - \alpha)\phi_2^2),$$
$$\rho_B = 2((1 - \alpha)\phi_1^2 + \alpha\phi_2^2).$$

This system was chosen to monitor the performance of the TF and W approximations at increasing overlaps between densities $\rho_A$ and $\rho_B$ due to rather localized character of $\phi_1$ and $\phi_2$. Increase of the parameter $\alpha$ in the range $0 < \alpha < 0.5$ correlates with the increase of the overlap. Our previous analyses of these approximations showed that these approximations fail at large overlaps\textsuperscript{31–33} where the overlap increase was achieved by shortening the distance between the interacting subsystems. The presently considered system provides an alternative way to control the amount of the overlap without changing the geometry but by changing the parameter $\alpha$.

Figure 2(a) shows the non-additive kinetic potential for $\alpha = 0.99$, what means that the target density is localized mainly on lithium with a small admixture of the density on helium. The potential exhibits a barrier between the nuclei and a value shift in the vicinity of lithium. It is evident from the plot that the value of the shift is equal to the difference between orbital energies $\Delta \varepsilon = \varepsilon_{2s} - \varepsilon_{1s}$. Thus, the role of it is to equalize the ground-state one-electron energy levels in each of the two potential wells. Obviously, the exact potential has to decay from the shifted level to zero somewhere beyond the presented scope. Unfortunately, the reconstructed potential is not able to capture this range accurately due to poor description of the density by basis function in this asymptotic region. Decreasing the mixing parameter causes that the target density is more and more localized on helium. This is reflected in the
FIG. 1. \( v^{\text{nad}}(r) \) for the beryllium atom. Exact potential (solid line), Thomas-Fermi approximation (dotted line), von Weizsäcker approximation (dashed line). Left column: (a) \( \alpha = 0.99 \), (b) \( \alpha = 0.9 \), (c) \( \alpha = 0.75 \), (d) \( \alpha = 0.5 \) Right column: (e) \( \alpha = 0.25 \), (f) \( \alpha = 0.1 \), (g) \( \alpha = 0.01 \), (h) \( \alpha = 0.001 \).
FIG. 2. \( v_{	ext{nad}}(r) \) for He (−0.95 Å) – Li\(^+\) (+0.95 Å). Exact potential (solid line), Thomas-Fermi approximation (dotted line), von Weizsäcker approximation (dashed line). Left column: (a) \( \alpha = 0.99 \), (b) \( \alpha = 0.9 \), (c) \( \alpha = 0.75 \), (d) \( \alpha = 0.5 \) Right column: (e) \( \alpha = 0.25 \), (f) \( \alpha = 0.1 \), (g) \( \alpha = 0.01 \), (h) \( \alpha = 0.001 \).
non-additive kinetic potential as the barrier becomes higher and narrower and moves toward the position of the node in $\phi_2$ at approximately 0.67 Å (Figs. 2(b)–2(h)). Additionally, the potential in the vicinity of the lithium nucleus falls with the decrease of $\alpha$.

The behaviour of potentials obtained from TF and W approximations is analogous to the beryllium case. The $\tilde{v}_i^{\text{nad}(T)}(r)$ does not resemble the exact potential anywhere. The $\tilde{v}_i^{\text{nad}(W)}(r)$ is able to reproduce barriers if the overlap between $\rho_A$ and $\rho_B$ is small, i.e., if $\alpha$ is close to 0 or 1. Nevertheless, it does not yield the potential value shift and produces spurious wells. For the strongest overlap ($\alpha = 0.5$), the W potential disappears completely.

Figure 2 shows how the non-additive kinetic potential depends on the mixing parameter, which controls the character of the target and frozen densities and the overlap between them. When the target density consists mostly of the valence part of the target and frozen densities and the overlap between them is a bit shifted with respect to the outer region. If the density of $\phi_3$ is admixed instead of the core density (Fig. 4(d)), then the barriers are much higher and narrower. Additionally, the shift between the barriers is not discernible as the difference between $\varepsilon_3$ and $\varepsilon_2$ is small. Taking the target density composed mostly of $\phi_3$ with a small admixture of core density (Fig. 4(e)) yields two overlapping bumps in $\tilde{v}_i^{\text{nad}(r)}$. If a small share of the density of $\phi_2$ is added instead (Fig. 4(e)), the bumps become spikes, which overlap as well.

In general, the performance of TF and W approximations is similar as for beryllium and He-Li$^+$. The $\tilde{v}_i^{\text{nad}(T)}(r)$ has cusps, which are more pronounced on the nuclei where the target density is small in comparison with the total density. Barriers in the exact non-additive kinetic potential are well reproduced by the W approximation, but it fails in other regions, especially where it becomes negative. The last case (Fig. 4(f)) is worth a more detailed analysis. If the target density is relatively negligible at the nucleus, two spikes overlap and merge practically to a one broad barrier with a split top. Although this effect is recovered by $\tilde{v}_i^{\text{nad}(W)}(r)$, the TF approximation seems to be reasonable in this region as well. The barrier is too broad and too high, but qualitatively it serves the same role, as it pushes out the target density, prohibiting its collapse on the nucleus. This is a typical situation in practical FDET based calculations, where the target density is well separated and does not penetrate deeply the density of the frozen subsystem. This is an explanation, why the TF approximation works reasonably well in practice, although it does not incorporate the exact features of $\tilde{v}_i^{\text{nad}(r)}$ in the vicinity of nuclei.

C. BeH$_2$

The beryllium hydride is a covalently bonded system comprising six electrons in three KS orbitals. The lowest orbital $\phi_1$ describes mainly the core electrons of the beryllium atom and its energy is $\varepsilon_1 = -3.85$ a.u. The second orbital $\phi_2$ has the $\sigma_g$ symmetry and the corresponding eigenvalue is $\varepsilon_2 = -0.31$ a.u. The third orbital $\phi_3$ has the energy $\varepsilon_3 = -0.27$ a.u. and $\sigma_u$ symmetry. Orbitals $\phi_2$ and $\phi_3$ are delocalized bonding orbitals between hydrogens and the beryllium atom. The partitioning of the density (Eq. (11)) is now the following:

$$\rho_A = 2(\alpha_1 \phi_1^2 + \alpha_2 \phi_2^2 + \alpha_3 \phi_3^2),$$
$$\rho_B = 2((1 - \alpha_1) \phi_1^2 + (1 - \alpha_2) \phi_2^2 + (1 - \alpha_3) \phi_3^2),$$

where $\alpha_1 + \alpha_2 + \alpha_3 = 1$.

Figures 4(a) and 4(b) show the non-additive kinetic potential, if the target density is composed mainly of the beryllium’s core electrons with small admixtures of the second and third orbital densities. These potentials are very similar, as they have a plateau in the beryllium’s nucleus region, which transforms into a bump and then smoothly drops to zero. If the target is taken as the density of the second orbital with a small admixture of core electrons density (Fig. 4(c)), $v_i^{\text{nad}}(r)$ has high barriers between hydrogens and beryllium and its value between them is a bit shifted with respect to the outer region. If the density of $\phi_3$ is admixed instead of the core density (Fig. 4(d)), then the barriers are much higher and narrower. Additionally, the shift between the barriers is not discernible as the difference between $\varepsilon_3$ and $\varepsilon_2$ is small. Taking the target density composed mostly of $\phi_3$ with a small admixture of core density (Fig. 4(e)) yields two overlapping bumps in $v_i^{\text{nad}(r)}$. If a small share of the density of $\phi_2$ is added instead (Fig. 4(e)), the bumps become spikes, which overlap as well.

D. Be-H$_2$ and B$^+$-H$_2$

The selected systems, Be-H$_2$ (A) and B$^+$-H$_2$ (B), consist of a hydrogen molecule at a fairly large distance (4.0 Å) from either a beryllium atom or a boron cation. Both system are in $C_{2v}$ symmetry and comprise six electron in three KS orbitals. As the separation is large, one orbital is localized mostly on the hydrogen molecule and the remaining two are localized on the beryllium or boron. What distinguishes these systems is the order of orbital levels. In Be-H$_2$ the orbital representing the hydrogen $\phi_{H_2}^A$ has a corresponding eigenvalue $\varepsilon_{H_2}^A = -0.38$ a.u., what places it between the levels of beryllium $\phi_{Be(1)}^A$ and $\phi_{Be(2)}^A$, with eigenvalues $\varepsilon_{Be(1)}^A = -3.90$ a.u. and $\varepsilon_{Be(2)}^A = -0.21$ a.u., respectively. If beryllium atom is replaced by a boron cation the order changes and the hydrogen’s orbital $\phi_{H_2}^B$ becomes the highest one with $\varepsilon_{H_2}^B = -0.38$ a.u. The orbitals localized on boron $\phi_{B(1)}^B$ and $\phi_{B(2)}^B$ have corresponding orbital energies $\varepsilon_{B(1)}^B = -7.10$ a.u. and
FIG. 3. Dependence of $\nu_{\text{nad}}(r)$ on the internuclear separation for He-Li$^+$. Helium nucleus is fixed at 0.0 Å, lithium nucleus in the range 0.5 Å–4.0 Å. Exact potential (solid line), Thomas-Fermi approximation (dotted line), von Weizsäcker approximation (dashed line).

$\epsilon^B_{B^{+}(2)} = -0.71$ a.u. Additionally, in case of B$^+$$-$$\text{H}_2$, the orbital localized mostly on the hydrogen molecule has a more pronounced tail on the other nucleus, composed mainly of boron’s $p_z$ orbital.

For both systems, the target density $\rho_A$ is chosen to consist mainly of the hydrogen orbital’s density (99%) with small admixture of densities of orbitals localized on beryllium or boron. Thus, the partitioning of the total density for Be-$\text{H}_2$...
reads
\[
\rho_A = 2(0.99\phi_{H_2}^A)^2 + \alpha_1^A (\phi_{Be(1)}^A)^2 + \alpha_2^A (\phi_{Be(2)}^A)^2, \\
\rho_B = 2(0.01\phi_{H_2}^B)^2 + (1-\alpha_1^A)(\phi_{Be(1)}^B)^2 + (1-\alpha_2^A)(\phi_{Be(2)}^B)^2,
\]
and for B+H₂
\[
\rho_A = 2(0.99\phi_{H_2}^A)^2 + \alpha_1^B (\phi_{H^+e(1)}^B)^2 + \alpha_2^B (\phi_{H^+e(2)}^B)^2, \\
\rho_B = 2(0.01\phi_{H_2}^B)^2 + (1-\alpha_1^B)(\phi_{H^+e(1)}^B)^2 + (1-\alpha_2^B)(\phi_{H^+e(2)}^B)^2,
\]
where \(\alpha_1 + \alpha_2 = 0.01\).

Figure 5 show non-additive kinetic potentials for different choices of the admixed density, represented by \(\alpha_1\) and \(\alpha_2\) parameters (Eqs. (18) and (19)). For both systems, when the core electrons density is admixed only (Figs. 5(a) and 5(d)), \(v_{nadv}^r(r)\) consists essentially of a value shift with a bumps on its edges, which smoothly decay to zero. The region for which the value is shifted is larger for beryllium, as the core orbital of boron is more confined due to higher nuclear charge. Due to non-negligible boron’s \(p_z\) component in \(\phi_{H_2}^B\), the bumps in the resulting non-additive kinetic potential are not symmetric, as the outer one is noticeably higher.

Taking \(\rho_A\), where admixture is composed of even shares of orbital densities (Figs. 5(b) and 5(e)), results in the increase of the bumps in \(v_{nadv}^r(r)\). The region between them remains shifted, as the core electrons density is still present in \(\rho_A\), but more density has to be pushed away from the surrounding region. The asymmetry of bumps for the system with boron becomes more evident. If the admixture in the target density

FIG. 4. \(v_{nadv}^r(r)\) for BeH₂. Exact potential (solid line), Thomas-Fermi approximation (dotted line), von Weizsäcker approximation (dashed line). Top: (a) \(\alpha_1 = 0.99, \alpha_2 = 0.01, \alpha_3 = 0.00\), (b) \(\alpha_1 = 0.99, \alpha_2 = 0.00, \alpha_3 = 0.01\), Middle: (c) \(\alpha_1 = 0.01, \alpha_2 = 0.99, \alpha_3 = 0.00\), (d) \(\alpha_1 = 0.00, \alpha_2 = 0.99, \alpha_3 = 0.01\), Bottom: (e) \(\alpha_1 = 0.01, \alpha_2 = 0.00, \alpha_3 = 0.99\), (f) \(\alpha_1 = 0.00, \alpha_2 = 0.01, \alpha_3 = 0.99\).
FIG. 5. $v_{\text{nad}}(r)$ for Be-H$_2$ (left column) and B$^+$-H$_2$ (right column). Exact potential (solid line), Thomas-Fermi approximation (dotted line), von Weizsäcker approximation (dashed line). Left column: (a) $\alpha_A^1 = 0.01, \alpha_A^2 = 0.00$, (b) $\alpha_A^1 = 0.005, \alpha_A^2 = 0.005$, (c) $\alpha_A^1 = 0.00, \alpha_A^2 = 0.01$. Right column: (d) $\alpha_B^1 = 0.01, \alpha_B^2 = 0.00$, (e) $\alpha_B^1 = 0.005, \alpha_B^2 = 0.005$, (f) $\alpha_B^1 = 0.00, \alpha_B^2 = 0.01$.

IV. CONCLUSIONS

The growing interest in applications of FDET based methods for multiscale molecular modeling is far ahead of the progress in the development of approximations to the non-additive kinetic energy functional, which is the key element of this theory. One of the legitimate routes to improve it is to identify the exact properties of its functional derivative, the non-additive kinetic potential, and to build them into new approximations. Although the alternative strategies circumventing the use of the approximations for the bi-functional $v_{\text{nad}}^{\mu}(\rho_A, \rho_B)(r)$ are attracting increased interests recently, they can be applied only if $\rho_B$ and the total electron density are obtained using some approximate methods to solve the Schrodinger equations in Born-Oppenheimer approximation.

does not comprise core electrons at all (Figs. 5(c) and 5(f)), the non-additive kinetic potentials exhibit barriers around the nucleus. For Be-H$_2$, the barriers have delta-like features, as they are high and narrow. In the B$^+$-H$_2$ case, the barriers are much lower and broader, what results in their overlap at the nucleus.

The approximate non-additive kinetic potentials are plotted in Fig. 5 as well. In comparison with the systems discussed so far, they show exactly the same desirable features, as well as the unwanted ones. The von Weizsäcker approximation yields barriers in correct positions and of proper height, but it produces spurious wells around them. The Thomas-Fermi potential is always positive, but it gives cusps at nuclei, which usually do not coincide with the position of barriers in the exact $v_{\text{nad}}^{\mu}(r)$. 
approximation. In multiscale simulations, FDET provides the formal framework for methods outside such restrictions. See, for example, the method proposed recently\textsuperscript{25} and in which $\rho_{B}$ is not associated with any system described within the Born-Oppenheimer approximation because it is an ensemble averaged quantity. For this reason, the development of good approximations for the bifunctional is a key condition for reliable applications of FDET in practice. The present work serves this purpose by providing exact reference potentials in chemically important scenarios supplemented by the analysis of strengths and weaknesses of two “parent” approximations to the kinetic energy, namely the Thomas-Fermi and von Weizsäcker functionals, as potential building blocks for deriving the approximation for the bifunctional $v_{\text{eff}}^{\text{ref}}(\rho_{A}, \rho_{B})(r)$. Obtaining reference potentials for pairs of electron densities seems to be a very promising strategy. In the present work, the reference potentials are constructed for prototypical pairs of densities, which represent various possibilities of partitioning of the total density into frozen and target subsystems. Target densities $\rho_{A}$ are always two-electron and spin-compensated, in order to construct the corresponding Kohn-Sham potential $v_{K}(\rho_{A})$ analytically. Although this approach rules out the possibility to study larger molecular systems, it circumvents some of the problems intrinsic to numerical inversion procedures, and still enables to grasp the most crucial features of the exact potential. The reference potentials obtained for the model systems show the role of $v_{\text{eff}}^{\text{ref}}(r)$ in shaping the embedded orbitals. This work reveals that the constraint due to the presence of the frozen density manifests itself by the barriers and by shifts in the Kohn-Sham potential is some regions of space. The presence of barriers is a local effect, the role of which is to push out the density from a confined fragment of space. The role of shift is to control the amount of the target density that overlaps strongly with the frozen density. It is a non-local effect, which depends on the difference between one-electron energy levels. The shifts and barriers feature also in the potentials reported by Savin and Wesolowski\textsuperscript{42} for an one-electron energy levels. The shifts and barriers appear as a common feature in realistic molecular systems.

This work reveals strong and weak points of two fundamental approximations to the kinetic energy functional, namely the Thomas-Fermi and von Weizsäcker approximation. The von Weizsäcker approximation is able to reproduce barriers when the target and frozen densities do not overlap much. In case of strong overlap it fails completely. The Thomas-Fermi approximation does not exhibit any of the characteristic features of the exact non-additive kinetic potential. Nevertheless, its cusps push out some of the target density from the nucleus when it is needed. In the intermediate regions $v_{\text{eff}}^{\text{TF}}(\rho_{A}, \rho_{B})(r)$ produces spurious wells, which can affect very much the densities optimized with it. The TF approximation is more regular in this respect. None of the approximations can reproduce shifted regions in the potential.

The presented reference potentials should serve as a guideline for constructing new approximations. The main conclusion of this work is that the full von Weizsäcker term is very important in some regions of space, whereas adding it in others should be highly avoided. This conclusion has already been exploited in the NDSD approximation to the bifunctional $v_{\text{eff}}^{\text{ref}}(\rho_{A}, \rho_{B})(r)$ in which the full von Weizsäcker term is added near nuclei. The present work suggests that it may be also needed somewhere in the intermolecular regions.

ACKNOWLEDGMENTS

This work was supported by the International Ph.D.-studies program at the Faculty of Chemistry Jagiellonian University within the Foundation for Polish Science MPD Program co-financed by the EU European Regional Development Fund and the Grant from Swiss National Science Foundation (Grant No. 200020/134791/1).