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# The energy-differences based exact criterion for testing approximations to the functional for the kinetic energy of non-interacting electrons

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## Abstract

Gradient-dependent approximations to the functional of the kinetic energy of non-interacting electrons ( $T_s[\rho]$ ), which reflect various properties of the exact functional, are considered. For specially constructed pairs of electron densities, for which the analytic expression for the differences of  $T_s[\rho]$  is known, it is shown that the accuracy of the quantities derivable from a given approximation to  $T_s[\rho]$ : energy differences and their functional derivatives, does not reflect that of  $T_s[\rho]$  itself. The comparisons between the exact values of the kinetic energy in such cases are proposed as an independent condition/criterion for appraisal of approximations to  $T_s[\rho]$ .

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(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

In the quest for an orbital-free method to study many-electron systems initiated in the works of Thomas [1] and Fermi [2], an universally applicable approximation to the kinetic energy as density functional ( $T[\rho]$ ) remains an unsolved issue. The functional  $T_s[\rho]$  [3, 4] of the kinetic energy of non-interacting electrons is strongly related to this quest. For molecular or atomic systems, the differences between the two functionals are rather small [5]. Approximations to  $T_s[\rho]$  are not needed in the Kohn–Sham formulation of density functional theory [6, 7] because of the availability of the Kohn–Sham orbitals. This successful formal framework, although not orbital-free, could be converted into the orbital-free method if both  $T_s[\rho]$  and the exchange–correlation energy functional could be reasonably approximated by means of explicit density functionals. Currently, orbital-free methods are not robust enough to be nearly

as universally applicable as the Kohn–Sham equations based ones [8, 9]. The exchange–correlation energy functional is a minor component of the total energy, whereas the kinetic energy is a major one. Whereas even the simplest approximations to the exchange–correlation energy functional applied within the Kohn–Sham framework lead to a reasonable description of many important properties of atoms, molecules, and solids, known approximations to  $T_s[\rho]$  used to approximate  $\frac{\delta T_s[\rho]}{\delta \rho}$  in variational orbital-free calculations lead usually to qualitatively wrong results [9–12]. Although an acceptable approximation to  $\frac{\delta T_s[\rho]}{\delta \rho}$  is the ultimate goal and an indispensable component of any successful orbital-free computational framework, related quantities are frequently subject of numerical comparisons instead. Most commonly, the kinetic energy itself, which is a global quantity, is subject of such analyses [8, 9, 13–15] or the density of the kinetic energy  $t_s$  ( $T_s[\rho] = \int t_s(\vec{r}) d\vec{r}$ ) [16, 17], which similarly to  $\frac{\delta T_s[\rho]}{\delta \rho}$  is a local quantity. It has to be underlined, however, that  $t_s$  is not defined uniquely. For a recent concise review of strategies to approximate  $T_s[\rho]$  and challenges involved see [18]. This makes the relation between accuracies of  $t_s^{\text{appr}}$  and  $\frac{\delta T_s^{\text{appr}}[\rho]}{\delta \rho}$  derived from a common approximation to  $T_s^{\text{appr}}[\rho]$  less straightforward. Since all quantities derived from  $T_s[\rho]$  would be exact if the approximation to  $T_s[\rho]$  were exact, it is tempting to assume that a good approximation to  $T_s[\rho]$  would also lead to good approximations to the related quantities: energy differences such as the non-additive kinetic energy bi-functional ( $T_s^{\text{nad}}[\rho_A, \rho_B] = T_s[\rho_A + \rho_B] - T_s[\rho_A] - T_s[\rho_B]$ ) and its functional derivatives ( $\frac{\delta T_s^{\text{nad}}[\rho_A, \rho_B]}{\delta \rho_X}$ , where  $X = A$  or  $B$ ). In view of the fact that relative errors in  $T_s[\rho]$  obtained from even the best approximations are in the range of 1%, this assumption should be put to scrutiny. In the present work, we analyse the differences of the kinetic energy and the associated functional derivatives. The exact numerical values of  $T_s^{\text{nad}}[\rho_A, \rho_B]$  for a pair of electron densities obtained from a particular partitioning of four-electron density is used to assess the practical usefulness of several approximations. Focusing the analysis on  $T_s^{\text{nad}}[\rho_A, \rho_B]$  arises from the following reasons.

- The energy differences are targets in numerical studies.
- Approximations to  $T_s^{\text{nad}}[\rho_A, \rho_B]$  are needed in practice in various types of calculations: (i) methods based on Hohenberg–Kohn variational principle, which use one-electron orbitals for all subsystems of the investigated subsystem as the basic descriptors [19, 20] (subsystem formulation of density functional theory by Cortona [19]); (ii) methods also based on Hohenberg–Kohn variational principle which, however, use one-electron orbitals only for a selected subsystem and the total electron density as basic descriptors (orbital-free embedding [21]); (iii) methods using orbital-free embedding effective potential in the linear-response density-functional-theory general framework to obtain excited states of embedded systems [25, 26]; (iv) conventional wavefunction based methods, in which the orbital-free embedding potential of [21] is used as an addition to the external potential [27, 28].
- $T_s^{\text{nad}}[\rho_A, \rho_B]$  disappears for non-overlapping pairs  $\rho_A$  and  $\rho_B$ . It is possible, therefore, to construct approximations to this quantity satisfying this additional condition designed for application in cases where the overlap between  $\rho_A(\vec{r})$  and  $\rho_B(\vec{r})$  is small. For such approximations, the magnitude of the electron density overlap thus provides the convenient applicability criterion.

Turning back to the subsystem formulation of density functional theory by Cortona [19], it can be considered as a possible alternative to Kohn–Sham calculations applying semi-local functionals in studies of intermolecular interactions. The repartition of the total electron density into  $\rho_A$  and  $\rho_B$  is the result of variational calculations. If an approximation to  $T_s^{\text{nad}}[\rho_A, \rho_B]$  is used instead of the exact functional this repartition is unique although

it is not for the exact case. Numerical experience shows that semi-local approximations to  $T_s^{\text{nad}}[\rho_A, \rho_B]$  lead to such repartition which minimizes the overlap between  $\rho_A$  and  $\rho_B$ . In the case of weakly bound intermolecular complexes, this repartition corresponds to the molecules forming the complex. As far as interaction energies and equilibrium geometries are concerned, local density approximation applied in Kohn–Sham calculations is known to lead to unsatisfactory results whereas the same approximation applied in the subsystem based calculations simultaneously for exchange-correlation- and non-additive kinetic components of the total energy leads to good results in many cases [22, 23]. This is probably the result of mutual cancellation of errors in the exchange- and kinetic energy contributions to the interaction energy in the weakly overlapping case. For the same reasons, the dissociation of such complexes, which are known to be wrongly described by semi-local Kohn–Sham calculations [24], can be expected to be better described by semi-local subsystem-based calculations.

Our previous analyses concerned the applicability of several semi-local approximations to  $T_s[\rho]$  in approximating the functional derivatives of  $T_s^{\text{nad}}[\rho_A, \rho_B]$  [29–31]. These studies showed that there is no correlation between the errors in  $T_s[\rho]$  and that of  $\frac{\delta T_s^{\text{nad}}[\rho_A, \rho_B]}{\delta \rho_X}$  for the considered approximations. The one with the largest domain of applicability was selected. In the absence of exact reference data for  $T_s^{\text{nad}}[\rho_A, \rho_B]$ , the origin of the lack of correlation between the errors of these closely related quantities could not be investigated further. The present work provides the missing link. Owing to the availability of the exact numerical data for  $T_s^{\text{nad}}[\rho_A, \rho_B]$ , where  $\rho_A$  and  $\rho_B$  are obtained from a particular partitioning of a four-electron density, the accuracy of  $T_s^{\text{nad}}[\rho_A, \rho_B]$  can be also analysed.

Throughout the text, we use the following convention: the symbols  $T_s[\rho]$ ,  $T_s^{\text{nad}}[\rho_A, \rho_B]$  and  $\frac{\delta T_s^{\text{nad}}[\rho_A, \rho_B]}{\delta \rho_A}$  denote the exact quantities. Approximated quantities indicated by means of the acronym of the approximation *appr* (*appr* = GEA0, GEA2, W, etc). The symbols  $\rho$ ,  $\rho_A$ ,  $\rho_B$  and  $\rho_X$  are used for unspecified functions. Any other index added to  $\rho$  indicates a specific electron density.

## 2. Numerical calculations

### 2.1. Exact reference data for $T_s^{\text{nad}}[\rho_A, \rho_B]$

We consider a spin-compensated four-electron systems, for which the ground-state electron density is *noninteracting pure-state v-representable*. Such system can be described by means of Kohn–Sham equations [6]. Throughout the text,  $\phi_1$  and  $\phi_2$  denote the two canonic Kohn–Sham orbitals i.e. one-electron functions solving Kohn–Sham equations. The orbitals  $\phi_1$  and  $\phi_2$  and the ground-state electron density are linked by a simple relation ( $\rho^{(4)} = 2|\phi_1|^2 + 2|\phi_2|^2$ ). For a particular partitioning of  $\rho^{(4)}$  into two spin-compensated components:  $\rho_\alpha^{(2)}$  and  $\rho_{\bar{\alpha}}^{(2)}$ , where

$$\rho_\alpha^{(2)} = \alpha \times 2 \times |\phi_1|^2 + (1 - \alpha) \times 2 \times |\phi_2|^2 \quad (1)$$

and

$$\rho_{\bar{\alpha}}^{(2)} = (1 - \alpha) \times 2 \times |\phi_1|^2 + \alpha \times 2 \times |\phi_2|^2 \quad (2)$$

where

$$0 \leq \alpha \leq 1$$

$T_s^{\text{nad}}[\rho_\alpha^{(2)}, \rho_{\bar{\alpha}}^{(2)}]$  can be expressed analytically as a consequence of the fact that for all involved densities the exact analytic expression for  $T_s[\rho]$  is available either as the von Weizsäcker

functional in the case of densities integrating to two electrons or as a sum of two von Weizsäcker terms for the ground-state density of the whole system [32].

$$T_s^{\text{nad}}[\rho_\alpha^{(2)}, \rho_{\bar{\alpha}}^{(2)}] = \int \frac{1}{8} f(\alpha) d\vec{r} \quad (3)$$

where

$$f(\alpha) = \frac{\rho_1^{\text{KS}} + \rho_2^{\text{KS}}}{\rho_1^{\text{KS}} \times \rho_2^{\text{KS}}} \times \frac{\alpha(1-\alpha) |\rho_1^{\text{KS}} \nabla \rho_2^{\text{KS}} - \rho_2^{\text{KS}} \nabla \rho_1^{\text{KS}}|^2}{\alpha(1-\alpha)((\rho_1^{\text{KS}})^2 + (\rho_2^{\text{KS}})^2) + \rho_1^{\text{KS}} \rho_2^{\text{KS}} (2\alpha^2 - 2\alpha + 1)}. \quad (4)$$

We underline that neither the exact Kohn–Sham effective potential nor the exact ground-state electron density is required to obtain  $\rho_1^{\text{KS}}$  and  $\rho_2^{\text{KS}}$ . Orbital densities  $\rho_1^{\text{KS}}$  and  $\rho_2^{\text{KS}}$  derived in calculations using any approximation for the exchange–correlation potential and any external potential add up to the total electron density, which is pure-state non-interacting  $v$ -representable by construction. Therefore, all relevant quantities  $T_s[\rho_1^{\text{KS}} + \rho_2^{\text{KS}}]$ ,  $T_s[\rho_1^{\text{KS}}]$ , and  $T_s[\rho_2^{\text{KS}}]$  are well defined.

## 2.2. Approximations to $T_s[\rho]$

In this work, we study the relations between the accuracy of closely related quantities:  $T_s[\rho]$ ,  $T_s^{\text{nad}}[\rho_A, \rho_B]$  and  $\frac{\delta T_s^{\text{nad}}[\rho_A, \rho_B]}{\delta \rho_X}$  obtained using the same approximated functional for the kinetic energy ( $T_s^{\text{appr}}[\rho]$ ) and the definitions of these quantities in the exact case:

$$T_s^{\text{nad(appr)}}[\rho_A, \rho_B] = T_s^{\text{appr}}[\rho_A + \rho_B] - T_s^{\text{appr}}[\rho_A] - T_s^{\text{appr}}[\rho_B] \quad (5)$$

$$\frac{\delta T_s^{\text{nad(appr)}}[\rho_A, \rho_B]}{\delta \rho_A} = \left. \frac{\delta T_s^{\text{appr}}[\rho]}{\delta \rho} \right|_{\rho=\rho_A+\rho_B} - \left. \frac{\delta T_s^{\text{appr}}[\rho]}{\delta \rho} \right|_{\rho=\rho_A}. \quad (6)$$

The group of considered approximations comprises semi-local functionals depending only on two quantities: electron density and its gradient. Such functionals are too simple for the purpose of orbital-free calculations as pointed out by several authors (see [9, 11] for instance). They are, however, of potential interest in approximating the effective potential in practice, either in fully variational calculations based on the subsystem formulation of density functional theory [19] or in partially variational calculations to obtain orbitals embedded in an orbital-free environment using one-electron equations (equations (20) and (21) in [21]).

Functionals of the following general form are considered:

$$T_s^{\text{appr}}[\rho] = \int \frac{3}{10} (3\pi^2)^{2/3} \rho^{5/3} F^{\text{appr}}(s) d\vec{r} \quad (7)$$

where  $s = \frac{|\nabla \rho|}{2\rho k_F}$  with  $k_F = (3\pi^2 \rho)^{1/3}$ , whereas the function  $F^{\text{appr}}(s)$  (*enhancement factor*) determines the gradient-dependence in each case:

$$F^{\text{GEO}}(s) = 1 \quad (8)$$

$$F^{\text{GEO2}}(s) = 1 + \frac{5}{27} s^2 = F^{\text{GEO}}(s) + \frac{5}{27} s^2 \quad (9)$$

$$\begin{aligned} F^{\text{OL1}}(s) &= 1 + \frac{5}{27} s^2 + 0.00677 \frac{20}{3} (3\pi^2)^{-1/3} s \\ &= F^{\text{GEO2}}(s) + 0.00677 \frac{20}{3} (3\pi^2)^{-1/3} s \end{aligned} \quad (10)$$

**Table 1.** The considered approximations to  $T_s[\rho]$ . GEA stands for gradient expansion approximation.

Formal origin	Acronym used	Reference
Electron gas with constant gradient and One-electron or two-electron spin compensated systems	W	von Weizsäcker [45]
uniform electron gas and zeroth order GEA	GEA0	Thomas and Fermi [1, 2]
Second-order GEA	GEA2	Kirzhnits [46]
Fourth-order GEA (selected terms)	E00	Ernzerhof [47]
Sixth-order GEA (selected terms)	P92	Perdew [48]
Second-order GEA + scaling properties for higher orders	OL1	Ou-Yang and Levy [49]
Second-order GEA + scaling properties for higher orders	OL2	Ou-Yang and Levy [49]
Conjointnes conjecture	LC94	Lembarki and Chermette [44]

$$\begin{aligned}
F^{\text{OL2}}(s) &= 1 + \frac{5}{27}s^2 + \frac{0.0887}{C_F} \frac{2(3\pi^2)^{1/3}s}{1 + 8(3\pi^2)^{1/3}s} \\
&= F^{\text{GEA2}}(s) + \frac{0.0887}{C_F} \frac{2(3\pi^2)^{1/3}s}{1 + 8(3\pi^2)^{1/3}s}
\end{aligned} \tag{11}$$

$$F^{\text{LC94}}(s) = \frac{1 + 0.093\,907s \operatorname{arcsinh}(76.32s) + (0.266\,08 - 0.080\,9615 e^{-100s^2})s^2}{1 + 0.093\,907s \operatorname{arcsinh}(76.32s) + 0.577\,67 \times 10^{-4}s^4} \tag{12}$$

$$\begin{aligned}
F^{\text{P92}}(s) &= \frac{1 + 88.396s^2 + 16.3683s^4}{1 + 88.2108s^2} \\
&= F^{\text{GEA2}}(s) + \frac{1}{27} \frac{0.0004s^2 + 0.8901s^4}{1 + 88.2108s^2}
\end{aligned} \tag{13}$$

$$F^{\text{E00}}(s) = \frac{135 + 28s^2 + 5s^4}{135 + 3s^2} = F^{\text{GEA2}}(s) + \frac{40}{9} \frac{s^4}{135 + 3s^2} \tag{14}$$

$$F^{\text{W}}(s) = \frac{5}{3}s^2. \tag{15}$$

Except for  $T_s^{\text{LC94}}[\rho]$ , the analytic form of all considered functional reflects certain exact properties of  $T_s[\rho]$  (see table 1). One of the objectives of the present study, is to determine, if obeying/violating exact properties affects the quality of the investigated quantities:  $T_s^{\text{appr}}[\rho]$ ,  $T_s^{\text{nad(appr)}}[\rho_A, \rho_B]$ , and  $\frac{\delta T_s^{\text{nad}}[\rho_A, \rho_B]}{\delta \rho_X}$ . The functionals  $T_s^{\text{GEA0}}[\rho]$  and  $T_s^{\text{GEA2}}[\rho]$  representing the zeroth- and second-order gradient expansion of  $T_s[\rho]$  are considered here as the basis for comparisons with other approximations. The functionals  $T_s^{\text{OL1}}[\rho]$ ,  $T_s^{\text{OL2}}[\rho]$ ,  $T_s^{\text{P92}}[\rho]$  and  $T_s^{\text{E00}}[\rho]$  differ from  $T_s^{\text{GEA2}}[\rho]$  by additional terms representing contributions due to higher orders. A common property of all the functionals in this group is the correct uniform electron gas limit. Additionally, the  $T_s^{\text{LC94}}[\rho]$  and  $T_s^{\text{W}}[\rho]$  functionals are included in this survey. The analytic form of  $T_s^{\text{LC94}}[\rho]$  is based on an ad hoc assumption ('conjointnes conjecture' [33]).  $T_s^{\text{LC94}}[\rho]$  provides a very good approximation to the functional derivative of  $T_s^{\text{nad}}[\rho_A, \rho_B]$  as shown in dedicated studies of the accuracy of the corresponding functional derivative for weakly overlapping pairs  $\rho_A$  and  $\rho_B$  in model systems [29, 30].  $T^{\text{W}}[\rho]$  represents the dominant term in an alternative strategy to approximate  $T_s[\rho]$  which is not based on uniform electron gas but on other systems.  $T_s^{\text{W}}[\rho]$  is the exact functional for one- or spin-compensated two-electron systems. Divided by 9, however, it equals the second-order

contribution ( $\frac{1}{72} \frac{|\nabla\rho|^2}{\rho}$ , represented by  $\frac{5}{27}s^2$  in equation (9)) in the gradient expansion of  $T_s[\rho]$ . The atomic or molecular electron densities do not vary slowly and comprise usually more than two electrons. Therefore, the choice of either  $T_s^W[\rho]$  or  $T_s^{\text{GEO}}[\rho]$  as the starting point in building up an approximation for  $T_s[\rho]$  ( $\lambda$  versus  $\gamma$  controversy [14]) should be verified in practice as it is made in this work concerning  $T_s^{\text{nad}}[\rho_A, \rho_B]$ .

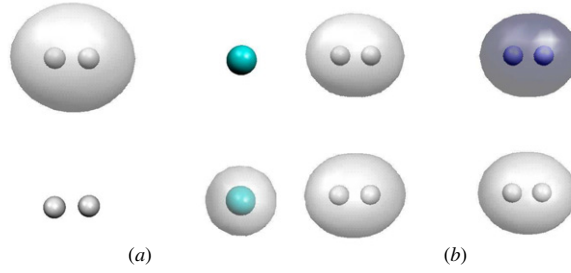
### 2.3. The considered four-electron systems

The analytic expression for  $T_s^{\text{nad}}[\rho_\alpha, \rho_{\bar{\alpha}}]$  given in equation (3) holds for any pair  $\rho_\alpha$  and  $\rho_{\bar{\alpha}}$  obtained from the proposed decomposition of the electron density in a spin-compensated four-electron systems. It is worthwhile to note that any external potential and any approximation to the exchange-correlation potential can be used for this purpose. We underline that, for each particular choice for the external potential and for the approximation to the exchange-correlation potential used in the Kohn–Sham equations to obtain the four-electron density,  $\rho_1^{\text{KS}}$  and  $\rho_2^{\text{KS}}$  used in equation (3) are not defined uniquely because the two generating Kohn–Sham orbitals can be subject to an unitary transformation. In view of possible multitude of pairs  $\rho_\alpha$  and  $\rho_{\bar{\alpha}}$  of chemical relevancy, we focus our demonstration of applicability of equation (3) as a quality criterion for approximations to  $T_s[\rho]$  on a small number of cases. They correspond to various types of intermolecular complexes, in which the overlap between the orbital densities in such systems varies considerably. We underline that systems, which dissociate into two spin-compensated two-electron fragments, are representative for a more general situation as far as the density overlap is concerned. We note that far from molecular centre the behaviour of the electron density is known to be determined by the highest occupied Kohn–Sham orbital. Therefore, the density overlap in the case of a sufficiently separated two two-electron systems is also representative for densities comprising more than two electrons in each subsystem.

The doubly-occupied pairs of orbitals ( $\phi_1$  and  $\phi_2$ ) used to construct  $\rho_1^{\text{KS}}$  and  $\rho_2^{\text{KS}}$  are derived from Kohn–Sham calculations applying local density approximation for the functional of the exchange-correlation energy [34–36] and the cc-pVDZ<sup>1</sup> [37] basis sets. The considered external potentials correspond to the following complexes: (i) linear H<sub>2</sub>–H<sub>2</sub> ( $d_{\text{eq}} = 6.50$  Bohr and  $d_{\text{eq}}(\text{H–H}) = 1.4$  Bohr [38]), (ii) T-shaped H<sub>2</sub>–H<sub>2</sub> ( $d_{\text{eq}} = 6.50$  Bohr and  $d_{\text{eq}}(\text{H–H}) = 1.4$  Bohr [38]), (iii) He–He ( $d_{\text{eq}}=5.6$  Bohr [39]), (iv) linear He–H<sub>2</sub> ( $d_{\text{eq}} = 6.33$  Bohr,  $d_{\text{eq}}(\text{H–H}) = 1.4$  Bohr [39]), (v) T-shaped He–H<sub>2</sub> ( $d_{\text{eq}} = 6.33$  Bohr,  $d_{\text{eq}}(\text{H–H}) = 1.4$  Bohr [39]), (vi) linear Li<sup>+</sup>–H<sub>2</sub> ( $d_{\text{eq}} = 3.86$  Bohr,  $d(\text{H–H})=1.4$  Bohr [40]), (vii) T-shaped Li<sup>+</sup>–H<sub>2</sub> ( $d_{\text{eq}} = 3.86$  Bohr,  $d(\text{H–H})=1.4$  Bohr [40]), (viii) Li<sup>+</sup>–He ( $d_{\text{eq}} = 3.61$  Bohr [41]).  $d_{\text{eq}}$  denotes either the distance between the two closest atoms from different subsystems in the case of linear complexes or the distance between the centre of the H<sub>2</sub> molecule and the closest atom from the other subsystem in the case of T-shaped complexes. Throughout the text, the label ‘T’ is used to indicate the T-shaped arrangement of molecules. The arrangement is linear otherwise.

The numerical results are obtained using the program deMon2K [42] modified for the purposes of this work. The program parameters are set as follows: GRID FIXED FINE, SCFTYPE TOL = 10<sup>−8</sup>, ERIS TOL = 10<sup>−14</sup>, DIIS OFF, AUXIS(GEN-A4\*).

<sup>1</sup> Basis sets were obtained from the Extensible Computational Chemistry Environment Basis Set Database, Version 02/25/04, as developed and distributed by the Molecular Science Computing Facility, Environmental and Molecular Sciences Laboratory which is part of the Pacific Northwest Laboratory, PO Box 999, Richland, WA 99352, USA, and funded by the US Department of Energy. The Pacific Northwest Laboratory is a multi-program laboratory operated by Battelle Memorial Institute for the US Department of Energy under contract DE-AC06-76RLO 1830. Contact David Feller or Karen Schuchardt for further information, <http://www.emsl.pnl.gov/forms/basisform.html>, 2004.



**Figure 1.** The two extreme cases of localization of orbital densities ( $\rho_A = 2 |\phi_1|^2$  and  $\rho_B = 2 |\phi_2|^2$ ) considered in this work: (a) well-localized Kohn–Sham orbitals for  $\text{Li}^+\text{-H}_2$  and (b) delocalized Kohn–Sham orbitals in the  $\text{H}_2\text{-H}_2$  complex. In each figure, the lower and upper parts show  $\phi_1$  and  $\phi_2$ , respectively.

**Table 2.** Relative errors of  $T_s[\rho_0^{(4)}]$  (in %) obtained using various approximations at equilibrium distance for the considered four-electron systems (for the used acronyms, see table 1).

System	W	GEO0	GEO2	E00	P92	OL1	OL2	LC94
$\text{H}_2\text{-H}_2$	-0.176	-10.447	0.645	5.277	0.667	1.564	1.287	-0.295
$\text{H}_2\text{-H}_2\text{-T}$	-0.271	-10.441	0.640	5.232	0.662	1.559	1.283	-0.291
$\text{He-He}$	-0.100	-10.536	0.564	4.110	0.587	1.551	1.216	0.193
$\text{He-H}_2$	-0.087	-10.517	0.585	4.444	0.607	1.553	1.234	0.053
$\text{He-H}_2\text{-T}$	-0.144	-10.512	0.583	4.415	0.606	1.552	1.233	0.056
$\text{Li}^+\text{-H}_2$	-0.617	-9.880	1.162	4.575	1.184	2.141	1.818	0.742
$\text{Li}^+\text{-H}_2\text{-T}$	-0.909	-9.822	1.188	4.535	1.210	2.165	1.844	0.785
$\text{Li}^+\text{-He}$	-0.509	-10.061	0.994	4.255	1.016	1.981	1.649	0.653
Average	-0.352	-10.277	0.795	4.605	0.817	1.758	1.446	0.384

### 3. Results and discussions

Among the studied systems are such, where the orbitals  $\phi_1$  and  $\phi_2$  are localized in different regions in real space or such, where both  $\phi_1$  and  $\phi_2$  extend over the whole system (see figure 1). In the former case, the overlap between the orbital densities ( $\rho_1^{\text{KS}}$  and  $\rho_2^{\text{KS}}$ ) is small and it diminishes rapidly with increasing intermolecular distance reaching zero at the dissociation limit, whereas their overlap is strong in the latter one. The accuracy of  $T_s^{\text{appr}}[\rho]$ ,  $T_s^{\text{nad(appr)}}[\rho_A, \rho_B]$  and  $\frac{\delta T_s^{\text{nad(appr)}}[\rho_A, \rho_B]}{\delta \rho_X}$ , where the label *appr* is used to identify one among the considered approximations listed in table 1, is analysed in separate sections below.

#### 3.1. Kinetic energy: $T_s[\rho]$

Table 2 collects the relative errors of the kinetic energy calculated using each of the considered approximate functionals for the considered four-electron systems. The exact values of  $T_s[\rho]$  are obtained analytically using the available Kohn–Sham orbitals.

$T_s^{\text{GEO0}}[\rho]$  underestimates systematically  $T_s[\rho]$  by about 10%, whereas  $T_s^{\text{GEO2}}[\rho]$  reduces this error significantly, which is in line with trends reported in other surveys [5]. As expected, all gradient-dependent functionals perform better than  $T_s^{\text{GEO0}}[\rho]$ . It is worthwhile to note, however, that  $T_s^{\text{GEO2}}[\rho]$  performs better than the non-empirical functionals of the generalized gradient approximation form constructed taking into account selected contributions due to



the fourth- and sixth order ( $T_s^{E00}[\rho]$  and  $T_s^{P92}[\rho]$ , respectively). None of the additional terms derived from scaling conditions present in  $T_s^{OL1}[\rho]$  and  $T_s^{OL2}[\rho]$  leads to any improvement as compared to  $T_s^{GEA2}[\rho]$ . For the von Weizsäcker functional ( $T^W[\rho]$ ), the errors in  $T_s[\rho]$  are the smallest. This indicates that the electron density in the considered systems deviates only slightly from the sum of the isolated two-electron components. The  $T_s^{LC94}[\rho]$  functional leads to errors of similar magnitude but opposite sign.

### 3.2. Kinetic energy differences: $T_s^{\text{nad}}[\rho_\alpha, \rho_{\bar{\alpha}}]$

In this section, we compare the numerical values of  $T_s^{\text{nad}}[\rho_\alpha, \rho_{\bar{\alpha}}]$  calculated by means of the exact expression (equations (3) and (4)) with their counterparts calculated for the same pairs of electron densities but using approximated functionals ( $T_s^{\text{nad(appr)}}[\rho_\alpha, \rho_{\bar{\alpha}}]$ ).

We start the analysis with the small overlap cases i.e. choosing  $\alpha = 1$  and such complexes for which the orbital densities:  $\rho_1^{\text{KS}}$  and  $\rho_2^{\text{KS}}$  are well-separated in space:  $\text{Li}^+-\text{H}_2$ ,  $\text{Li}^+-\text{He}$  and  $\text{He}-\text{H}_2$ . In such systems, the overlap between  $\rho_A$  and  $\rho_B$  is small even at equilibrium intermolecular distance and it decreases rapidly at larger separations. At intermediate intermolecular distances, the exact condition  $T_s^{\text{nad}}[\rho_{\alpha=1}, \rho_{\bar{\alpha}=0}] = 0$ , which holds for any external potential i.e. for any intermolecular distance (see equations (3) and (4)), is violated by the considered approximations. The numerical values of errors in  $T_s^{\text{nad(appr)}}[\rho_{\alpha=1}, \rho_{\bar{\alpha}=0}]$  are non-negligible although they are typically smaller in magnitude than the energy of interaction between the subsystems. The von Weizsäcker functional, although it leads to the smallest errors in  $T_s[\rho]$  discussed in the previous section, provides the worst approximation to  $T_s^{\text{nad}}[\rho_A, \rho_B]$ .

The analytic forms of  $T_s^{\text{nad}}[\rho_A, \rho_B]$  obtained using the  $T_s^{\text{GEO0}}[\rho]$  and  $T_s^W[\rho]$  approximations read

$$T_s^{\text{nad(GEO0)}}[\rho_A, \rho_B] = C_{TF} \int ((\rho_A + \rho_B)^{5/3} - \rho_A^{5/3} - \rho_B^{5/3}) d\vec{r} \quad (16)$$

$$T_s^{\text{nad(W)}}[\rho_A, \rho_B] = -\frac{1}{8} \int \frac{|\rho_A \nabla \rho_B - \rho_B \nabla \rho_A|^2}{\rho_A \rho_B (\rho_A + \rho_B)} d\vec{r} \leq 0. \quad (17)$$

Except the for zero-overlap case, neither  $T_s^{\text{nad(GEO0)}}[\rho_A, \rho_B]$  nor  $T_s^{\text{nad(W)}}[\rho_A, \rho_B]$  disappear.  $T_s^{\text{nad(GEO0)}}[\rho_A, \rho_B]$  is non-negative, whereas  $T_s^{\text{nad(W)}}[\rho_A, \rho_B]$  is non-positive. Therefore, the exact condition  $T_s^{\text{nad}}[\rho_{\alpha=1}, \rho_{\bar{\alpha}=0}] = 0$  cannot be satisfied by neither term if the overlap is nonzero. Due to non-negativity of  $T_s^{\text{nad(GEO0)}}[\rho_A, \rho_A]$ , it can also be used as a convenient measure of the magnitude of the overlap between  $\rho_A$  and  $\rho_B$ . Indeed, this quantity decreases rapidly with distance (see the numerical values for  $\text{Li}^+-\text{H}_2$ , collected in table 3). Since the GEO0 and von Weizsäcker contributions to  $T_s^{\text{nad}}[\rho_A, \rho_A]$  differ in sign, the second-order expansion (GEA2) is usually a better approximation to this quantity than GEO0.

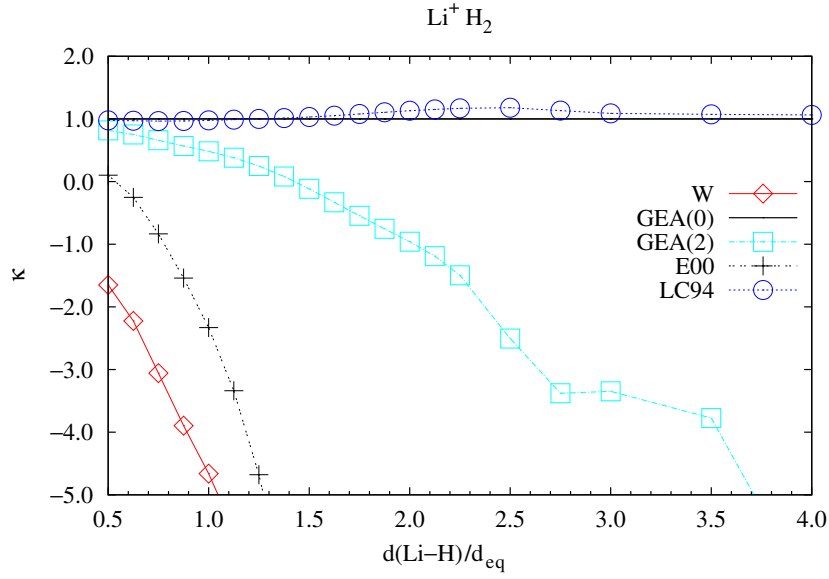
All remaining approximations (OL1, OL2, E00, P92 and LC94) comprise the common non-negative component  $T_s^{\text{nad(GEO0)}}[\rho_A, \rho_B]$ , which disappears only at zero overlap.

In order to discuss the possible improvement (or deterioration) upon  $T_s^{\text{GEO0}}[\rho]$  of the numerical values of  $T_s^{\text{nad}}[\rho_A, \rho_B]$  resulting from introduction of gradient-dependence into  $T_s^{\text{appr}}[\rho]$ , we introduce a dimensionless quantity  $\kappa^{\text{appr}}$  defined as

$$\kappa^{\text{appr}} = \frac{T_s^{\text{nad(appr)}}[\rho_A, \rho_B]}{T_s^{\text{nad(GEO0)}}[\rho_A, \rho_B]}, \quad (18)$$

for each considered approximation.

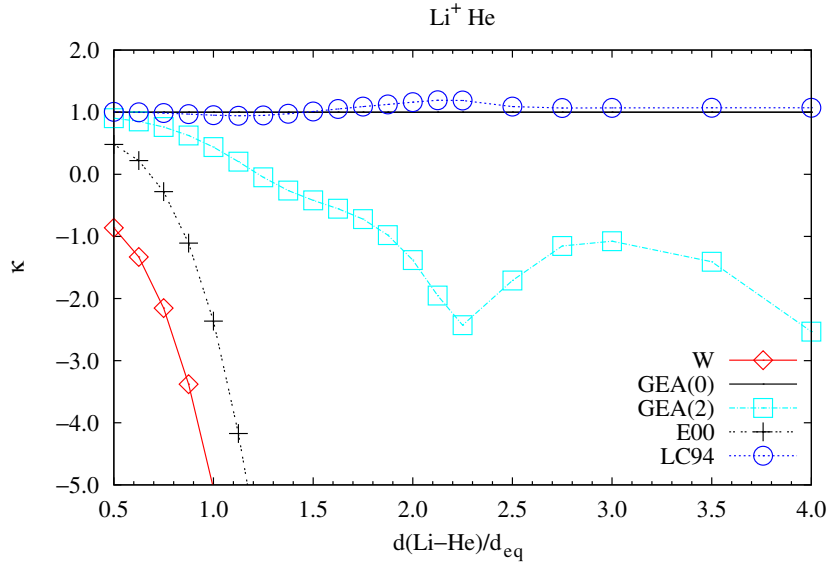
Figure 2 shows the variation of  $\kappa^{\text{appr}}$  with intermolecular distance for  $\text{Li}^+-\text{H}_2$ . The results obtained by means of the von Weizsäcker functional are also included to show the failure



**Figure 2.** The effect of introducing gradients to approximate  $T_s[\rho]$  on the accuracy of  $T_s^{\text{nad}}[\rho_A, \rho_B]$  in  $\text{Li}^+\text{-H}_2$  at various  $\text{Li-H}$  separations ( $\kappa^{\text{appr}} = \frac{T_s^{\text{nad}(\text{appr})}[\rho_A, \rho_B]}{T_s^{\text{nad}(\text{GEA0})}[\rho_A, \rho_B]}$ ,  $d_{\text{eq}} = 3.86$  Bohr). See table 1 for acronyms for each approximation. At the exact functional limit,  $T_s^{\text{nad}}[\rho_A, \rho_B] = 0$  and  $\kappa = 0$ . The P92, OL1 and OL2 results are not shown because they could not be distinguished from the GEA2 ones in the figure.

**Table 3.**  $T_s^{\text{nad}}[\rho_\alpha, \rho_{\bar{\alpha}}]$  (in Hartree) with  $\alpha = 1$ , obtained using the considered approximations (for the used acronyms, see table 1) at various distances between  $\text{Li}^+$  and  $\text{H}_2$  ( $d_{\text{eq}} = 3.86$  Bohr). At  $\alpha = 1$ , the exact value of  $T_s^{\text{nad}}[\rho_\alpha, \rho_{\bar{\alpha}}]$  equals zero.

Dist	W	GEA0	GEA2	E00	P92	OL1	OL2	LC94
0.500d <sub>eq</sub>	-0.392 497	0.237 955	0.194 344	0.024 387	0.194 254	0.195 341	0.196 046	0.232 661
0.625d <sub>eq</sub>	-0.224 930	0.101 117	0.076 125	-0.025 457	0.076 073	0.076 548	0.076 851	0.098 270
0.750d <sub>eq</sub>	-0.132 602	0.043 362	0.028 628	-0.036 179	0.028 598	0.028 806	0.028 940	0.041 872
0.875d <sub>eq</sub>	-0.082 094	0.021 075	0.011 953	-0.032 476	0.011 934	0.012 043	0.012 105	0.020 381
1.000d <sub>eq</sub>	-0.051 028	0.010 948	0.005 279	-0.025 509	0.005 267	0.005 330	0.005 358	0.010 693
1.125d <sub>eq</sub>	-0.031 313	0.005 616	0.002 137	-0.018 752	0.002 130	0.002 166	0.002 178	0.005 548
1.250d <sub>eq</sub>	-0.018 926	0.002 797	0.000 695	-0.013 089	0.000 690	0.000 710	0.000 715	0.002 796
1.375d <sub>eq</sub>	-0.011 225	0.001 358	0.000 111	-0.008 701	0.000 108	0.000 118	0.000 121	0.001 376
1.500d <sub>eq</sub>	-0.006 517	0.000 649	-0.000 075	-0.005 516	-0.000 077	-0.000 071	-0.000 070	0.000 669
1.625d <sub>eq</sub>	-0.003 701	0.000 309	-0.000 102	-0.003 344	-0.000 103	-0.000 100	-0.000 100	0.000 325
1.750d <sub>eq</sub>	-0.002 059	0.000 148	-0.000 081	-0.001 947	-0.000 081	-0.000 080	-0.000 080	0.000 160
1.875d <sub>eq</sub>	-0.001 125	0.000 071	-0.000 054	-0.001 096	-0.000 054	-0.000 053	-0.000 053	0.000 079
2.000d <sub>eq</sub>	-0.000 608	0.000 034	-0.000 033	-0.000 604	-0.000 033	-0.000 033	-0.000 033	0.000 039
2.125d <sub>eq</sub>	-0.000 329	0.000 017	-0.000 020	-0.000 331	-0.000 020	-0.000 020	-0.000 020	0.000 019
2.250d <sub>eq</sub>	-0.000 182	0.000 008	-0.000 012	-0.000 184	-0.000 012	-0.000 012	-0.000 012	0.000 009
2.500d <sub>eq</sub>	-0.000 067	0.000 002	-0.000 005	-0.000 067	-0.000 005	-0.000 005	-0.000 005	0.000 002
2.750d <sub>eq</sub>	-0.000 035	0.000 001	-0.000 003	-0.000 034	-0.000 003	-0.000 003	-0.000 003	0.000 001
3.000d <sub>eq</sub>	-0.000 023	0.000 001	-0.000 002	-0.000 023	-0.000 002	-0.000 002	-0.000 002	0.000 001
3.500d <sub>eq</sub>	-0.000 011	0.000 000	-0.000 001	-0.000 011	-0.000 001	-0.000 001	-0.000 001	0.000 000
4.000d <sub>eq</sub>	-0.000 004	0.000 000	-0.000 000	-0.000 004	-0.000 000	-0.000 000	-0.000 000	0.000 000



**Figure 3.** The effect of introducing gradients to approximate  $T_s[\rho]$  on the accuracy of  $T_s^{\text{nad}}[\rho_A, \rho_B]$  in  $\text{Li}^+ - \text{He}$  at various Li–He separations ( $\kappa^{\text{appr}} = \frac{T_s^{\text{nad}}(\text{appr})[\rho_A, \rho_B]}{T_s^{\text{nad}}(\text{GEO})[\rho_A, \rho_B]}$ ,  $d_{\text{eq}} = 3.61$  Bohr). See table 1 for acronyms for each approximation. At the exact functional limit,  $T_s^{\text{nad}}[\rho_A, \rho_B] = 0$  and  $\kappa = 0$ . The P92, OL1 and OL2 results are not shown because they could not be distinguished from the GEA2 ones in the figure.

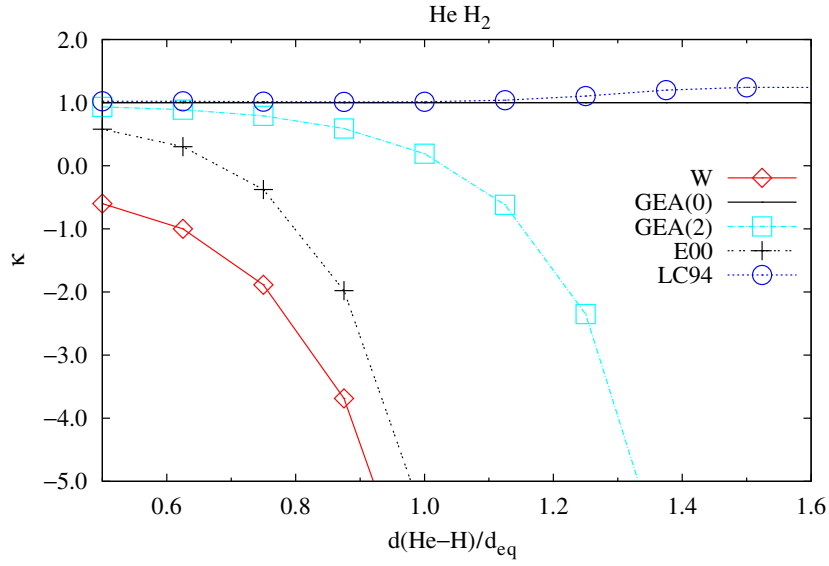
of this approximation. The  $T_s^{\text{nad}}[\rho_A, \rho_B]$  values derived using the  $T_s^{\text{OL1}}[\rho]$ ,  $T_s^{\text{OL2}}[\rho]$ ,  $T_s^{\text{P92}}[\rho]$  and  $T_s^{\text{GEA2}}[\rho]$  functionals are indistinguishable. Since all these functionals comprise the second-order component ( $T_s^{\text{GEA2}}[\rho]$ ), the above results indicate that the beyond-second-order terms in  $T_s^{\text{OL1}}[\rho]$ ,  $T_s^{\text{OL2}}[\rho]$  and  $T_s^{\text{P92}}[\rho]$  do not contribute noticeably to  $T_s^{\text{nad}}[\rho_A, \rho_B]$ . The E00 approximation leads, however, to qualitative different behaviour. At small inter-subsystem distances, the numerical values of  $T_s^{\text{nad}}[\rho_A, \rho_B]$  are even better than those obtained using either  $T_s^{\text{GEO}}[\rho]$  or  $T_s^{\text{GEA2}}[\rho]$ . The errors increase, however, rapidly with decreasing overlap (inter-subsystem distance). Comparing the GEA2, E00 and P92 results shows that the contributions to  $T_s^{\text{nad}}[\rho_A, \rho_B]$ , which are derived from the gradient-dependent terms in the fourth- and sixth-order in gradient expansion, cancel each other.

The GEA2, OL1, OL2 and P92 approximations improve upon GEA0 due to the common GEA2 term, for the reasons discussed before (opposite signs). Unfortunately, at very small overlaps the negative component due to the von Weizsäcker contribution prevails leading to negative errors in  $T_s^{\text{nad}}[\rho_A, \rho_B]$ . The magnitude of this negative contribution is only slightly (at most 0.0001 Hartree) larger than that due to GEA0.

The LC94 way of including gradients does not lead to better results than local density approximation (the numerical values of  $\kappa^{\text{LC94}}$  are close to 1). The distinct feature of  $T_s^{\text{LC94}}[\rho]$  is that performs rather uniformly in approximating  $T_s^{\text{nad}}[\rho_A, \rho_B]$  in the whole range of considered  $\rho_A - \rho_B$  overlaps.

The results for other cases of well-separated Kohn–Sham orbitals show similar trends to those for  $\text{Li}^+ - \text{H}_2$  (see figures 3 and 4 for  $\text{Li}^+ - \text{He}$  and  $\text{He} - \text{H}_2$ ).

The results for weakly overlapping  $\rho_A$  and  $\rho_B$  indicate that local density approximation is a good starting point to approximate  $T_s^{\text{nad}}[\rho_A, \rho_B]$ . In the second order, the numerical values

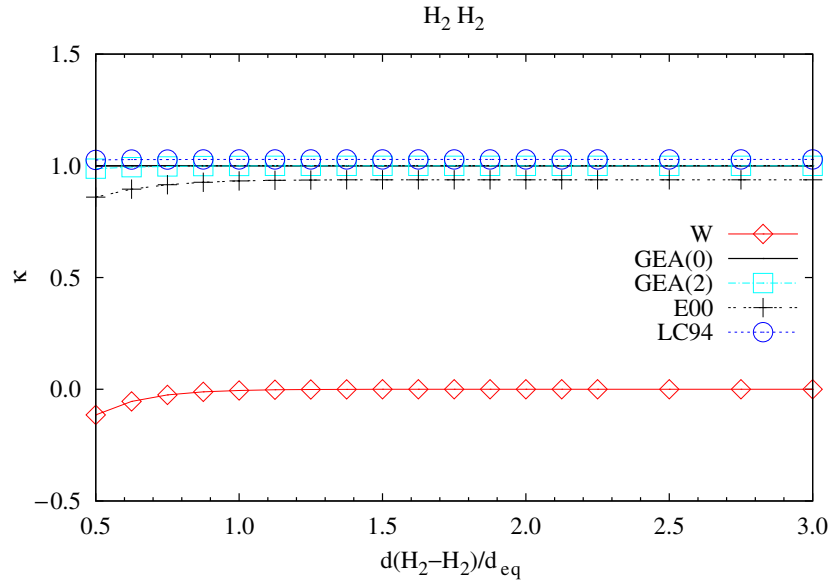


**Figure 4.** The effect of introducing gradients to approximate  $T_s[\rho]$  on the accuracy of  $T_s^{\text{nad}}[\rho_A, \rho_B]$  in He–H<sub>2</sub> at various He–H<sub>2</sub> separations ( $\kappa^{\text{appr}} = \frac{T_s^{\text{nad}(\text{appr})}[\rho_A, \rho_B]}{T_s^{\text{nad}(\text{GEA0})}[\rho_A, \rho_B]}$ ,  $d_{\text{eq}} = 6.33$  Bohr). See table 1 for acronyms for each approximation. At the exact functional limit,  $T_s^{\text{nad}}[\rho_A, \rho_B] = 0$  and  $\kappa = 0$ . The P92, OL1 and OL2 results are not shown because they could not be distinguished from the GEA2 ones in the figure.

of  $T_s^{\text{nad}}[\rho_A, \rho_B]$  are usually better than those due to the zeroth order. This improvement is, however, not universal because a systematic failure occurs at very small overlaps (negative contributions due to the second order). Going beyond the second order by means of taking into account selected higher order contributions does not solve this problem. They are numerically negligible (OL1, OL2, P92) or lead to even faster deterioration of the numerical values of  $T_s^{\text{nad}}[\rho_A, \rho_B]$  with decreasing overlap between  $\rho_A$  and  $\rho_B$  (the E00 case).

In the subsequent part, strongly overlapping pairs  $\rho_A$  and  $\rho_B$  are considered. In H<sub>2</sub>–H<sub>2</sub> or He–He, the Kohn–Sham orbitals extend over the same regions in space (see figure 1). For Li<sup>+</sup>–He, Li<sup>+</sup>–H<sub>2</sub> and He–H<sub>2</sub>, the initially well-separated orbital densities  $\rho_1^{\text{KS}}$  and  $\rho_2^{\text{KS}}$  are mixed using fractional values of the mixing factor  $\alpha$ . In the strong overlap cases, the von Weizsäcker functional represents a qualitative improvement over local density approximation as indicated by the numerical values of  $\kappa^W$  which are close to zero (see figures 5 and 6). The  $T_s^{\text{E00}}[\rho]$  functional also leads to better results than  $T_s^{\text{GEA0}}[\rho]$  but this improvement is less significant. The beyond-second-order contributions due to the special terms in OL1, OL2 and P92 approximations do not contribute to  $T_s^{\text{nad}}[\rho_A, \rho_B]$  noticeably. Moreover, the similarity between the GEA0 and GEA2 results indicates that the second-order contribution to  $T_s^{\text{nad}}[\rho_A, \rho_B]$  is also negligible if the densities  $\rho_A$  and  $\rho_B$  overlap significantly. The absolute errors in  $T_s^{\text{nad}}[\rho_\alpha, \rho_{\bar{\alpha}}]$  obtained by means of the  $T_s^{\text{LC94}}[\rho]$  functional are very similar.

According to equation (4), for  $0.0 \leq \alpha \leq 0.5$ ,  $T_s^{\text{nad}}[\rho_\alpha, \rho_{\bar{\alpha}}]$  is positive and monotonic function of  $\alpha$  reaching the maximum at  $\alpha = 0.5$  and this dependence is symmetric ( $T_s^{\text{nad}}[\rho_\alpha, \rho_{\bar{\alpha}}] = T_s^{\text{nad}}[\rho_{\bar{\alpha}}, \rho_\alpha]$ ). The dependence of  $T_s^{\text{nad}}[\rho_\alpha, \rho_{\bar{\alpha}}]$  on  $\alpha$  cannot be properly accounted for by means of the considered functionals. Compared to the exact results, a strong overestimation of  $T_s^{\text{nad}(\text{appr})}[\rho_{0.5}, \rho_{0.5}]$  takes place for all except the  $T_s^W[\rho]$  functional.

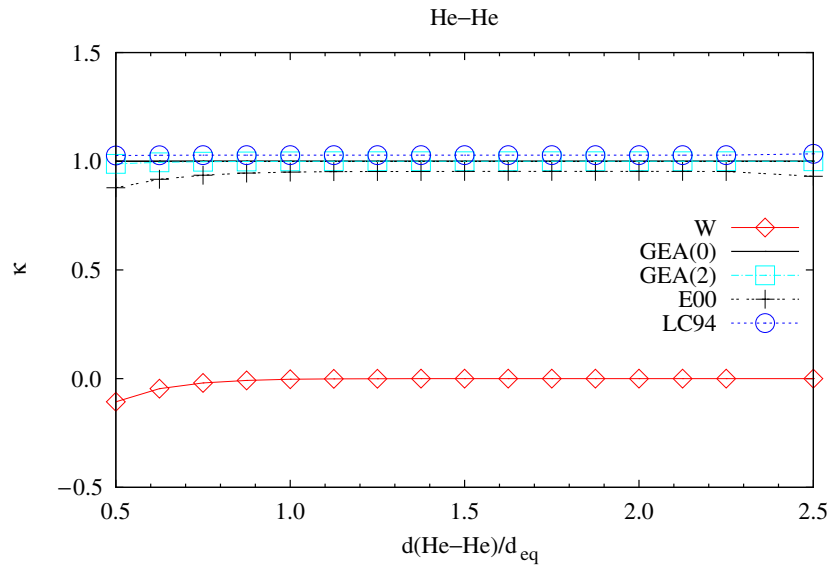


**Figure 5.** The effect of introducing gradients to approximate  $T_s[\rho]$  on the accuracy of  $T_s^{\text{nad}}[\rho_A, \rho_B]$  in  $\text{H}_2\text{-H}_2$  at various  $\text{H}_2\text{-H}_2$  separations ( $\kappa^{\text{appr}} = \frac{T_s^{\text{nad(appr)}}[\rho_A, \rho_B]}{T_s^{\text{nad(GEA0)}}[\rho_A, \rho_B]}$ ,  $d_{\text{eq}} = 6.50$  Bohr). See table 1 for acronyms for each approximation. At the exact functional limit,  $T_s^{\text{nad}}[\rho_A, \rho_B] = 0$  and  $\kappa = 0$ . The P92, OL1 and OL2 results are not shown because they could not be distinguished from the GEA2 ones on the figure.

**Table 4.**  $T_s^{\text{nad}}[\rho_\alpha, \rho_{\bar{\alpha}}]$  (in Hartree) obtained using the considered approximations (for the used acronyms, see table 1) and mixing of orbitals densities at equilibrium distance for  $\text{Li}^+\text{-H}_2$ .  $d_{\text{eq}} = 3.86$  Bohr).

$\alpha$	Exact	W	GEA0	GEA2	E00	P92	OL1	OL2	LC94
1.00	0.000 000	-0.051 028	0.010 948	0.005 279	-0.025 509	0.005 267	0.005 358	0.005 330	0.010 693
0.99	0.012 659	-0.038 369	0.130 517	0.126 254	0.083 832	0.126 245	0.127 198	0.127 192	0.136 397
0.90	0.032 249	-0.018 779	1.045 575	1.043 488	0.953 536	1.043 480	1.050 966	1.050 357	1.082 088
0.80	0.041 685	-0.009 342	1.807 585	1.806 547	1.694 367	1.806 538	1.819 451	1.817 914	1.863 410
0.70	0.047 136	-0.003 891	2.338 380	2.337 948	2.213 444	2.337 938	2.354 624	2.352 321	2.406 129
0.60	0.050 087	-0.000 941	2.652 527	2.652 422	2.521 410	2.652 412	2.671 328	2.668 537	2.726 910
0.50	0.051 027	-0.000 000	2.756 584	2.756 584	2.623 520	2.756 573	2.776 228	2.773 271	2.833 106

The errors in  $T_s^{\text{nad}}[\rho_\alpha, \rho_{\bar{\alpha}}]$  obtained using any approximation comprising the term derived from local density approximation (GEA0, GEA2, OL1, OL2, E00, P92) increase rapidly with increasing  $\alpha$  (see tables 4 and 5). The absolute errors in  $T_s^{\text{nad}}[\rho_\alpha, \rho_{\bar{\alpha}}]$  obtained using the von Weizsäcker functional are the smallest among the considered approximations but their sign is wrong. It can be shown easily that  $T_s^{\text{nad(W)}}[\rho_\alpha, \rho_{\bar{\alpha}}] - T_s^{\text{nad}}[\rho_\alpha, \rho_{\bar{\alpha}}] = T_s^{\text{nad(W)}}[\rho_1^{\text{KS}}, \rho_2^{\text{KS}}]$  i.e. the error in  $T_s^{\text{nad}}[\rho_\alpha, \rho_{\bar{\alpha}}]$  is  $\alpha$ -independent for this functional. The numerical results confirm the above relation within  $1\mu$  Hartree, which reflects the accuracy of the numerical integration in the procedures applied in this work. Similar trends occur for other systems, for  $\text{Li}^+\text{-H}_2$ :  $T_s^{\text{nad}}[\rho_{0.5}, \rho_{0.5}] = 0.051\,027$  Hartree (exact result),  $T_s^{\text{nad(GEA2)}}[\rho_{0.5}, \rho_{0.5}] = 2.756\,584$  Hartree



**Figure 6.** The effect of introducing gradients to approximate  $T_s[\rho]$  on the accuracy of  $T_s^{\text{nad}}[\rho_A, \rho_B]$  in He–He at various He–He separations ( $\kappa^{\text{appr}} = \frac{T_s^{\text{nad(appr)}}[\rho_A, \rho_B]}{T_s^{\text{nad(GEA0)}}[\rho_A, \rho_B]}$ ,  $d_{\text{eq}} = 5.60$  Bohr). See table 1 for acronyms for each approximation. At the exact functional limit,  $T_s^{\text{nad}}[\rho_A, \rho_B] = 0$  and  $\kappa = 0$ . The P92, OL1 and OL2 results are not shown because they could not be distinguished from the GEA2 ones on the figure.

**Table 5.**  $T_s^{\text{nad}}[\rho_\alpha, \rho_{\bar{\alpha}}]$  (in Hartree) obtained using the considered approximations (for the used acronyms, see table 1) and mixing of orbitals densities at equilibrium distance for H<sub>2</sub>–H<sub>2</sub>.  $d_{\text{eq}} = 6.50$  Bohr.)

$\alpha$	Exact	W	GEA0	GEA2	E00	P92	OL1	OL2	LC94
1.00	0.000 000	−0.003 773	0.711 094	0.710 674	0.662 891	0.710 671	0.715 651	0.714 744	0.731 268
0.99	0.000 722	−0.003 050	0.711 098	0.710 759	0.663 637	0.710 756	0.714 829	0.715 736	0.731 272
0.90	0.002 252	−0.001 521	0.711 136	0.710 967	0.665 369	0.710 964	0.715 943	0.715 037	0.731 301
0.80	0.003 012	−0.000 761	0.711 169	0.711 084	0.666 289	0.711 081	0.716 061	0.715 155	0.731 330
0.70	0.003 455	−0.000 318	0.711 192	0.711 157	0.666 829	0.711 154	0.716 133	0.715 227	0.731 351
0.60	0.003 696	−0.000 077	0.711 206	0.711 197	0.667 119	0.711 195	0.716 174	0.715 268	0.731 364
0.50	0.003 773	−0.000 000	0.711 210	0.711 210	0.667 212	0.711 208	0.716 187	0.715 281	0.731 369

and  $T_s^{\text{nad(W)}}[\rho_{0.5}, \rho_{0.5}] = 0$ , whereas for He–H<sub>2</sub>:  $T_s^{\text{nad}}[\rho_{0.5}, \rho_{0.5}] = 0.003 353$  Hartree (exact result),  $T_s^{\text{nad(GEA2)}}[\rho_{0.5}, \rho_{0.5}] = 1.269 748$  Hartree and  $T_s^{\text{nad(W)}}[\rho_{0.5}, \rho_{0.5}] = 0$ .

In all cases, where  $\rho_A$  and  $\rho_B$  overlap strongly any approximate functional based on gradient expansion approximation is shown to fail qualitatively in approximating  $T_s^{\text{nad}}[\rho_A, \rho_B]$  due to the zeroth order. For instance, local density approximation leads to the error in  $T_s^{\text{nad}}[\rho_A, \rho_B]$  equal to 0.711 Hartree for H<sub>2</sub>–H<sub>2</sub> at equilibrium geometry at  $\alpha = 1$ , which represents a significant part (about 30%) of the kinetic energy of the isolated H<sub>2</sub> molecule. The von Weizsäcker functional leads to significantly smaller errors in  $T_s^{\text{nad}}[\rho_A, \rho_B]$  (the magnitude reaching 0.004 Hartree in the same case and the negative sign). This significant reduction of errors indicates that the von Weizsäcker functional provides probably a better starting point

to construct approximations to  $T_s^{\text{nad}}[\rho_A, \rho_B]$  than local density approximation for strongly overlapping pairs  $\rho_A$  and  $\rho_B$ .

### 3.3. The functional derivative: $\frac{\delta T_s^{\text{nad}}[\rho_A, \rho_B]}{\delta \rho_A}$

The functional derivative  $\frac{\delta T_s^{\text{nad(appr)}}[\rho_A, \rho_B]}{\delta \rho_X}(\vec{r})$  is a local quantity. It corresponds to one of the components of the effective potential in one-electron equations for embedded orbitals [21]. Opposite to the global quantities discussed so far such as  $T_s[\rho]$  and  $T_s^{\text{nad}}[\rho_A, \rho_B]$ , for which exact reference values could be obtained, no exact reference potential is available for the considered systems. We note, however, that the electron density ( $\rho_0^{(4)}$ ) derived from the Kohn–Sham calculations represents also the total electron density obtained from a coupled pair of two sets of coupled one-electron equations for embedded orbitals (equations (20) and (21) in [21]) provided the  $\frac{\delta T_s^{\text{nad(appr)}}[\rho_A, \rho_B]}{\delta \rho_X}(\vec{r})$  component of the effective potential in these equations is exact. Below, we denote the pair of electron densities derived from such equations as  $\rho_A^{\text{KSCED}}$  and  $\rho_B^{\text{KSCED}}$ . If an approximation is used for  $\frac{\delta T_s^{\text{nad(appr)}}[\rho_A, \rho_B]}{\delta \rho_X}(\vec{r})$ , the relation  $\rho_0^{(4)}(\vec{r}) = \rho_A^{\text{KSCED(appr)}}(\vec{r}) + \rho_B^{\text{KSCED(appr)}}(\vec{r})$  does not necessary hold and the differences between  $\rho_0^{(4)}$  and  $\rho_A^{\text{KSCED(appr)}} + \rho_B^{\text{KSCED(appr)}}$  can be used as indicators of quality of the applied used approximation [29–31]. It is convenient to discuss the differences between these electron densities using a global quantity  $M$  defined as

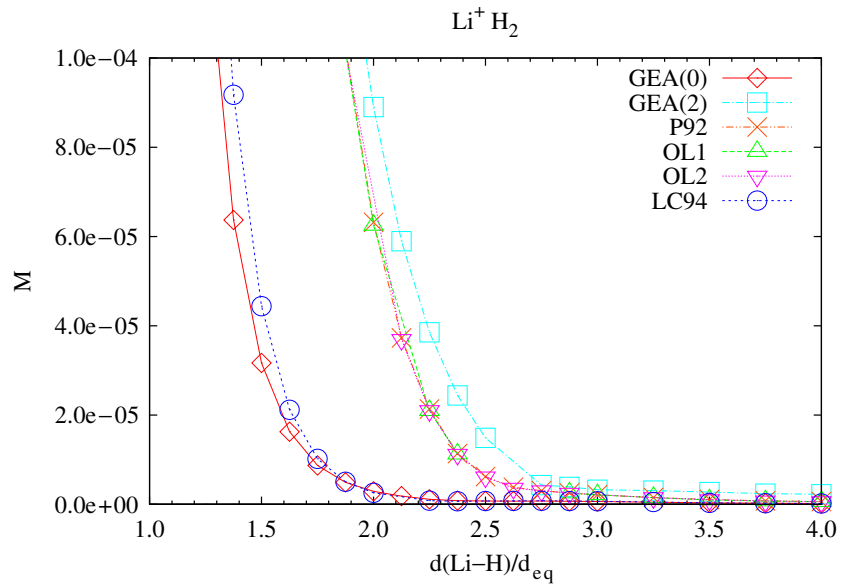
$$M^{\text{appr}} = \frac{1}{N} \sqrt{\int (\rho_0^{(4)}(\vec{r}) - (\rho_A^{\text{KSCED(appr)}}(\vec{r}) + \rho_B^{\text{KSCED(appr)}}(\vec{r})))^2 d\vec{r}}, \quad (19)$$

where  $N = 4$  in the present work.

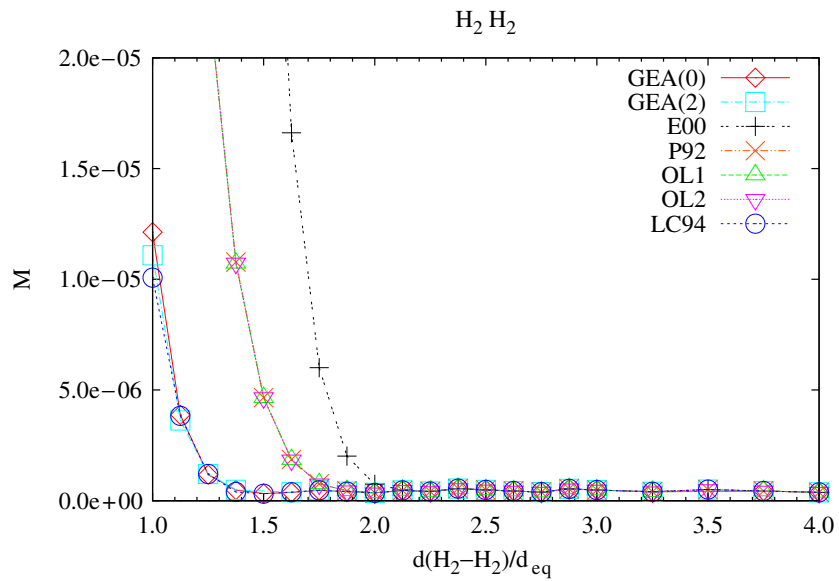
For the exact functional:

$$M^{\text{exact}} = 0. \quad (20)$$

It is worthwhile to note that  $\rho_A^{\text{KSCED(appr)}}$  and  $\rho_B^{\text{KSCED(appr)}}$  are not the same as the orbital densities discussed in the previous section because they are obtained from different equations. All the considered approximations satisfy the exact limit ( $T_s^{\text{nad}}[\rho_A, \rho_B] = 0$ ) at zero overlap between  $\rho_A$  and  $\rho_B$ . Therefore, possible errors in  $\frac{\delta T_s^{\text{nad(appr)}}[\rho_A, \rho_B]}{\delta \rho_X}$  should be looked for at small inter-subsystem distances, for which the overlap between  $\rho_A^{\text{KSCED(appr)}}$  and  $\rho_B^{\text{KSCED(appr)}}$  is large. Indeed, numerical values of  $M^{\text{appr}}$  confirm such behaviour as shown in figures 7 and 8 for two representative cases of  $\text{Li}^+-\text{H}_2$  and  $\text{H}_2-\text{H}_2$ . For different approximations, the deterioration of  $\frac{\delta T_s^{\text{nad(appr)}}[\rho_A, \rho_B]}{\delta \rho_X}$  with increasing overlap does not start at the same inter-subsystem distance. GEA0 appears to be the best as the critical point, at which  $M$  starts a rapid increase, occurs at the shortest inter-subsystem distances. LC94 results resemble closely the GEA0 ones. Other approximations are usually worse (increase in  $M^{\text{appr}}$ ). In the case of  $\text{Li}^+-\text{H}_2$  (see figure 7) and other systems comprising  $\text{Li}^+$  [43], GEA2 leads to larger errors in  $\frac{\delta T_s^{\text{nad(appr)}}[\rho_A, \rho_B]}{\delta \rho_X}$  than GEA0. For charged systems, a significant modification of the electron density of isolated subsystems can be expected to occur as the results of complexation. Since the changes of the electron density are determined by potentials, the electron density in such systems is prone to flaws of the approximation used for  $\frac{\delta T_s^{\text{nad}}[\rho_A, \rho_B]}{\delta \rho_X}$ . The deterioration of  $\frac{\delta T_s^{\text{nad}}[\rho_A, \rho_B]}{\delta \rho_X}$ , which follows replacing GEA0 by GEA2, is in line with similar trends reported for other systems characterized by large complexation induced changes of electron density [31]. It is probably the result of the spurious negative values  $T_s^{\text{nad(GEA2)}}[\rho_A, \rho_B]$  at small  $\rho_A-\rho_B$  overlaps. Interestingly, for non-polar systems GEA0 and GEA2 lead to very similar dependence on  $M$



**Figure 7.** The effect of errors in  $\frac{\delta T_s^{\text{nad}}[\rho_A, \rho_B]}{\delta \rho_X}$  for approximations to  $T_s[\rho]$  given in table 1 on the total electron density obtained from variational calculations for  $\text{Li}^+ - \text{H}_2$  at various distances  $d(\text{Li}-\text{H})$  ( $d_{\text{eq}} = 3.86$  Bohr). For the definition of measure  $M$ , see text.



**Figure 8.** The effect of errors in  $\frac{\delta T_s^{\text{nad}}[\rho_A, \rho_B]}{\delta \rho_X}$  for approximations to  $T_s[\rho]$  given in table 1 on the total electron density obtained from variational calculations for  $\text{H}_2 - \text{H}_2$  at various distances  $d(\text{H}-\text{H})$  ( $d_{\text{eq}} = 6.50$  Bohr). For the definition of measure  $M$ , see text.



on inter-subsystem distance as shown in figure 8 for H<sub>2</sub>–H<sub>2</sub> and [43] for other systems. It is worthwhile to recall that all four approximations to  $T_s[\rho]$ : GEA2, OL1, OL2 and P92, lead to almost indistinguishable values of  $T_s^{\text{nad}}[\rho_A, \rho_B]$  indicating that the beyond-second-order contributions to this quantity are negligible. Differences in  $M^{\text{appr}}$  indicate, however, that the functional derivatives of the corresponding terms are not negligible. These additional components of the potential are, however, not capable to correct the errors introduced by the contribution to  $\frac{\delta T_s^{\text{nad}}[\rho_A, \rho_B]}{\delta \rho_X}$  due to the von Weizsäcker terms in the second order. Other approximations (W, E00) lead to even worse approximations to  $\frac{\delta T_s^{\text{nad}}[\rho_A, \rho_B]}{\delta \rho_X}$ .

#### 4. Conclusions

In this work, we demonstrate that using a given approximation to  $T_s[\rho]$  to derive related quantities (energy differences and their derivatives) leads to errors, which do not correlate with those of the kinetic energy itself. Although, all quantities derivable from a given approximate expression for  $T_s[\rho]$  would become also exact if this expression were exact, the lack of correlation along the series

$$T_s[\rho] \longrightarrow T_s^{\text{nad}}[\rho_A, \rho_B] \longrightarrow \frac{\delta T_s^{\text{nad}}[\rho_A, \rho_B]}{\delta \rho_X}$$

indicates that a dedicated analysis of these quantities is not redundant because the known approximations to  $T_s[\rho]$  are very unsatisfactory. Therefore, we propose the analytic relations for  $T_s^{\text{nad}}[\rho_\alpha, \rho_{\bar{\alpha}}]$  valid for four-electron systems to be used as an additional criterion to be applied in development of approximations to  $T_s[\rho]$ . Especially the condition  $T_s^{\text{nad}}[|\phi_1|^2, |\phi_2|^2] = 0$  (where  $\phi_1$  and  $\phi_2$  are Kohn–Sham orbitals) is easily applicable. This condition holds for both the exact Kohn–Sham orbitals and orbitals derived from numerical calculations applying an approximate exchange–correlation potential in a closed-shell four-electron system. Although the above lack of correlation was demonstrated for gradient-dependent approximations only, the fact that enforcing various exact properties of the exact functional on the approximate ones leads to surprising behaviour of errors suggests that this criterion might be useful also in the development of approximations to  $T_s[\rho]$  which depends on other quantities than electron density and its gradient.

Comparisons between the reference results corresponding to exact quantities  $T_s^{\text{nad}}[\rho_A, \rho_B]$  and  $\frac{\delta T_s^{\text{nad}}[\rho_A, \rho_B]}{\delta \rho_X}$  with those obtained using approximate functionals in model four-electron systems allow us to address several issues of relevance to numerical simulations based on methods, which hinge on *easy-to-calculate* approximations to  $T_s^{\text{nad}}[\rho_A, \rho_B]$  such as the gradient-dependent ones considered in this work. These issues are addressed below.

*Domain of applicability of gradient-dependent approximations to  $T_s^{\text{nad}}[\rho_A, \rho_B]$ .* For strongly overlapping pairs  $\rho_A$  and  $\rho_B$ , all considered approximations fail to yield  $T_s^{\text{nad}}[\rho_A, \rho_B]$  and  $\frac{\delta T_s^{\text{nad}}[\rho_A, \rho_B]}{\delta \rho_X}$  of any practical value. The functionals comprising the zeroth-order gradient expansion term lead to significantly overestimated numerical values of  $T_s^{\text{nad}}[\rho_A, \rho_B]$  (the errors reaching almost the order of magnitude of the kinetic energy itself). The von Weizsäcker functional leads to significantly smaller errors in  $T_s^{\text{nad}}[\rho_A, \rho_B]$  but the quality of the corresponding functional derivatives is worse. For large overlaps, the development of an acceptable approximation to  $T_s^{\text{nad}}[\rho_A, \rho_B]$  (and  $\frac{\delta T_s^{\text{nad}}[\rho_A, \rho_B]}{\delta \rho_X}$ ) represent a task, which is comparable in difficulty to that in the  $T_s[\rho]$  (and  $\frac{T_s[\rho]}{\delta \rho}$ ) case.

If the overlap between  $\rho_A$  and  $\rho_B$  is small, as in the case the monomers in an intermolecular complex in the vicinity of the equilibrium geometry, the situation is less grim. The exact condition:  $T_s^{\text{nad}}[\rho_A, \rho_B] = 0$  at zero overlap is satisfied by all functionals considered in the present work by construction. In this simple way, the correct limit at infinitely separated subsystems is obeyed. At small but nonzero overlaps, already the local density approximation (zeroth-order gradient expansion) provides a good approximation to both  $T_s^{\text{nad}}[\rho_A, \rho_B]$  and  $\frac{\delta T_s^{\text{nad}}[\rho_A, \rho_B]}{\delta \rho_X}$ . Further improvements are possible by means of introduction of gradient-dependence.

*The starting point in constructing approximation to  $T_s^{\text{nad}}[\rho_A, \rho_B]$ — $\lambda$  versus  $\gamma$  controversy.* The numerical results indicate that the local density approximation (exact for the uniform electron gas) rather than von Weizsäcker functional (exact for one- or spin-compensated two-electron systems) is more useful as the starting point in approximating both  $T_s^{\text{nad}}[\rho_A, \rho_B]$  and  $\frac{\delta T_s^{\text{nad}}[\rho_A, \rho_B]}{\delta \rho_X}$  if the overlap between  $\rho_A$  and  $\rho_B$  is not significant. At large overlaps, the situation is reverse.

*Going beyond local density approximation.* Compared to local density approximation, the gradient-dependent contributions due to the second order do not affect the accuracy of  $T_s^{\text{nad}}[\rho_A, \rho_B]$  and  $\frac{\delta T_s^{\text{nad}}[\rho_A, \rho_B]}{\delta \rho_X}$  in a uniform way. The next to zeroth-order term in gradient expansion is proportional to  $s^2$  ( $s = \frac{|\nabla \rho|}{2\rho k_F}$ ). Reduced density gradients  $s$  are small near the nuclei, where the electron density is large, whereas they diverge far from the nuclei due to the exponential decay of the electron density. The fact that the numerical values of  $T_s^{\text{nad}}[\rho_A, \rho_B]$  improve noticeably if  $s^2$ -dependent term is included in the case of intermediate overlaps between  $\rho_A$  and  $\rho_B$  indicates that the presence of this term is desired. However, the same term leads to negative values of  $T_s^{\text{nad}}[\rho_A, \rho_B]$  at the smallest overlaps. In variational calculations, artificial attracting of electron density to regions with very small overlap might lead to problems. Indeed, the effect of  $s^2$ -dependent contributions on the accuracy of  $\frac{\delta T_s^{\text{nad}}[\rho_A, \rho_B]}{\delta \rho_X}$  is erratic as compared to local density approximation. This flaws of the second-order gradient expansion approximation are not corrected by such terms due to higher orders in the gradient expansion, which are derived from either scaling considerations or take into account higher powers of  $s$ . A pragmatic solution to this problem, proposed in [29, 30] is based on cutting off smoothly the contributions to  $T_s[\rho]$  due to large  $s$ . The enhancement factor in the kinetic functional by Lembarki and Chermette [44] was used for this purpose. The present study confirms the usefulness of this Ansatz. Moreover, owing to the availability of exact values of  $T_s^{\text{nad}}[\rho_A, \rho_B]$ , it is shown that  $T_s^{\text{LC94}}[\rho]$  appears to be the most robust among gradient-dependent functionals in approximating simultaneously all three associated quantities:  $T_s[\rho]$ ,  $T_s^{\text{nad}}[\rho_A, \rho_B]$  and  $\frac{\delta T_s^{\text{nad}}[\rho_A, \rho_B]}{\delta \rho_X}$ . Compared to local density approximation, the accuracy of  $T_s^{\text{LC94}}[\rho]$  is better, whereas  $T_s^{\text{nad(LC94)}}[\rho_A, \rho_B]$  and  $\frac{\delta T_s^{\text{nad(LC94)}}[\rho_A, \rho_B]}{\delta \rho_X}$  are about the same. This indicates that improvements are still possible within the group of gradient-dependent approximations applied for small  $\rho_A$ – $\rho_B$  overlaps.

*Importance of enforcing exact properties  $T_s[\rho]$ .* The effect of enforcing selected exact properties of the functional  $T_s[\rho]$  (GEA2, OL1, OL2, E00, and P92 approximations) on the accuracy of the related quantities is not systematic along the series  $T_s[\rho] \longrightarrow T_s^{\text{nad}}[\rho_A, \rho_B] \longrightarrow \frac{\delta T_s^{\text{nad}}[\rho_A, \rho_B]}{\delta \rho_X}$  in the case of small overlaps between  $\rho_A$  and  $\rho_B$ , i.e. in the most promising domain of applicability of gradient-dependent approximations. All the functionals

in this group are known to approximate  $T_s[\rho]$  better than zeroth-order gradient expansion. Unfortunately, these improvements are not passed on to  $T_s^{\text{nad}}[\rho_A, \rho_B]$  and subsequently to  $\frac{\delta T_s^{\text{nad}}[\rho_A, \rho_B]}{\delta \rho_X}$  in a systematic way. In particular, second-order gradient expansion leads to improvements in  $T_s^{\text{nad}}[\rho_A, \rho_B]$  in most cases but it does not improve  $\frac{\delta T_s^{\text{nad}}[\rho_A, \rho_B]}{\delta \rho_X}$ —worsening it even in some cases. Similar problems in using the second-order gradient expansion to approximate  $\frac{\delta T_s[\rho]}{\delta \rho}$  were reported [12]. The fact that the second-order expansion affects the accuracy of  $T_s^{\text{nad}}[\rho_A, \rho_B]$  and  $\frac{\delta T_s^{\text{nad}}[\rho_A, \rho_B]}{\delta \rho_X}$  in erratic way is attributed to the imbalance between the positive and negative errors due to zeroth- and second-order terms in the gradient expansion, which leads to negativity of  $T_s^{\text{nad}}[\rho_A, \rho_B]$  at the smallest overlaps. The higher orders terms derived from either scaling considerations (the  $T_s^{\text{OL1}}[\rho]$  and  $T_s^{\text{OL2}}[\rho]$  functionals) or taking into account higher powers of density gradients present in the gradient expansion approximation up to sixth order ( $T_s^{\text{P92}}[\rho]$ ) do not affect  $T_s^{\text{nad}}[\rho_A, \rho_B]$  noticeably although they affect  $\frac{\delta T_s^{\text{nad}}[\rho_A, \rho_B]}{\delta \rho_X}$ . They cannot, however, compensate the errors due to the second-order term in gradient expansion. The fourth-order-gradient-expansion-approximation based functional  $T_s^{\text{E00}}[\rho]$  performs rather poorly. It leads to a deterioration of the accuracy of  $\frac{\delta T_s^{\text{nad}}[\rho_A, \rho_B]}{\delta \rho_X}$  and rather erratic effect on the accuracy of  $T_s^{\text{nad}}[\rho_A, \rho_B]$ .

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