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Electron density errors and density-driven exchange-correlation energy errors in approximate density functional calculations

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Abstract

Since its formal introduction, density functional theory has achieved many successes on the fields of molecular and solid-state chemistry. According to its central theorems, the ground state of a many-electron system is fully described by its electron density, and the exact functional minimizes the energy at the exact electron density. For many years of density functional development, it was assumed that the improvements in the energy are accompanied by the improvements in the density, and the approximations approach the exact functional. In a recent analysis (Medvedev et al. *Science* **2017**, 355, 49-52.), it has been pointed out for fourteen first row (Be-Ne) atoms and cations with 2, 4, or 10 electrons that the nowadays popular flexible but physically less rigorous approximate density functionals may provide large errors in the calculated electron densities despite the accurate energies. Although far-reaching conclusions have been drawn in this work, the methodology used by the authors may need improvements. Most importantly, their benchmark set was biased towards small atomic cations with compressed, high electron densities. In our paper, we construct a molecular test set with chemically relevant densities and analyze the performance of several density functional approximations including the less-investigated double hybrids. We apply an intensive error measure for the density, its gradient, and its Laplacian and examine how the errors in the density propagate into the semi-local exchange-correlation energy. While we have confirmed the broad conclusions of Medvedev et al., our different way of analyzing the data has led to conclusions that differ in detail. Finally, seeking for a rationale behind the global hybrid or double hybrid methods from the density's point of view, we also analyze the role of the exact exchange and second-order perturbative correlation mixing in PBE-based global hybrid and double hybrid functional forms.

Introduction

Density functional theory is an essential tool in the electronic structure theory of molecules and materials, which provides accurate results at a low computational cost.^{1,2} According to the Hohenberg-Kohn theorems,³ the ground-state electron density uniquely determines the potential and thus contains all information about the system. There exists a universal density functional, which yields the exact ground-state energy of the system from its exact electron density variationally. In principle, the exact solution is possible using the simple one-electron Kohn-Sham equations⁴ since the potential of the physical interacting system can be replaced by the potential of a fictitious non-interacting system. The main difficulty is that a general form for the universal functional is not known. Several approximate functionals were constructed taking into account known physical properties of the exact exchange-correlation functional,^{5,6,7} but many were empirically fitted for databases with various chemical properties.^{8,9,10} The exchange and correlation parts are usually approximated together for systematic error

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cancellation.⁷ During the development, it was assumed that functionals with better energetics reproduce better the exact Kohn-Sham potential and thus produce better density.^{11,12,13} However, density functional approximations are close to the exact functional if they estimate well the exact Kohn-Sham potential.

There are several studies in the literature assessing the quality of the electron density and its derivatives obtained with various density functional approximations. For small molecules, Boyd et al. compared the electron density and its Laplacian at the bond critical point obtained from density functional and wave function calculations and found that three-parameter hybrid density functionals¹⁴ perform better than their semi-local parent functionals and much better than the local density approximation (LDA).¹⁵ Csonka et al.¹⁶ showed for the hydrogen molecule that the electron density can be accurately reproduced along the bond axis around the bond critical point by a proper mixing of the exact and semi-local exchange in a B3P86-type functional.^{17,18} The corresponding exact Kohn-Sham potential (v_{KS}) was also presented, which depends on the density (n), its gradient (∇n), its Laplacian ($\nabla^2 n$), and the energy of the (highest) occupied orbital (ε).¹⁹ (Note that this form is universal for two-electron spin-singlet systems.)

$$v_{KS}(\mathbf{r}) = -\frac{1}{8} \frac{(\nabla n)^2}{n^2} + \frac{1}{4} \frac{\nabla^2 n}{n} + \varepsilon \quad (1)$$

Furthermore, the errors of approximate Kohn-Sham potentials were analyzed in the bond critical point of the dissociating hydrogen molecule, where the exact Kohn-Sham potential is determined by the density, its Laplacian, and the energy of the (highest) occupied orbital since the gradient is zero.¹⁶ Bochevarov and Friesner compared the electron densities of small molecules obtained from self-consistent density functional calculations to full configuration interaction level reference densities.²⁰ They concluded that certain generalized gradient approximation (GGA) or three-parameter hybrid GGA¹⁴ functionals perform better with the empirically fitted OPTX exchange²¹ than with the original B88 exchange.¹⁷ Grabowski, Teale, et al. observed for standard local and semi-local functionals with the VWN5²² and LYP²³ correlation that the correlated densities (*i.e.*, the difference between the densities generated by the exchange-correlation method and the corresponding exchange-only method) and the correlation potentials are qualitatively incorrect, although the correlation may provide some error cancellation with the exchange part.²⁴ Grabowski, Fabiano, et al. also suggested the integral absolute density differences to measure the approximate density functional density errors radially in spherical atoms and along the bond axis in diatomic molecules.²⁵ According to the analysis of Tognetti and Joubert on 50 small molecules,²⁶ the electron density and its Laplacian at the bond critical point can be better described by the meta-GGA level TPSS functional²⁷ than by the GGA-level PBE functional.²⁸ However, the accuracy of the former can be achieved at the GGA-level by the empirically fitted HCTH functional, which was optimized also for some accurate exchange-correlation potentials.^{29,30,31} In contrast to the above mentioned studies, Cruz et al. showed that functionals which yield accurate energies often produce wrong potentials.³² Finally, Kim et al. argued that there are situations (*e.g.*, electron affinities) when the density-driven error (*i.e.*, the difference of the total energies evaluated on the approximate and the exact density) dominates over the functional error in the error of a variational density functional calculation.³³

Very recently, Medvedev et al. have reported that the unconstrained and highly empirical density functional construction with flexible functional forms can also bring farther from the exact functional as such functionals give accurate energies on wrong densities.³⁴ Their flexible functional form can be easily overfitted, which leads to oscillations in the exchange-correlation enhancement factor. These oscillations can propagate into the exchange-correlation potential and thus to the density.

Although this report met an intense response in the literature,^{35,36} it has been criticized how the authors arrived at their conclusion.^{37,38} In a comment,³⁷ Kepp pointed out that the benchmark set was strongly biased towards small atoms and atomic cations with $1s^2$ or $1s^2 2s^2$ electronic structure, and it is unclear if the description of the very compact electron densities in the atomic cations (with large dynamic

correlation) is chemically relevant. The test set seems to favor the hybrid functionals (*e.g.*, PBE0³⁹) since the Hartree-Fock (HF) exchange gives more accurate densities for two-electron systems. In a systemwise comparison, Kepp found a strong linear relationship between the errors in the ionic densities and the errors in the ionic energy differences computed by semi-local or hybrid functionals. In their response,⁴⁰ Medvedev et al. emphasized that the atoms and atomic cations were only intended to reveal internal problems in the methods, the ranking of the HF method is only mediocre because of its maximum error, and the relationship of the ionic densities and energy differences is evident as the density and energy errors each scales with the nuclear charge at constant electron number. Some other issues were collected by Korth.³⁸ For example, the all-electron coupled-cluster singles and doubles (CCSD) reference method in this benchmark might miss some core-valence correlation for systems with more than two electrons due to the missing triple or higher-order excitations, although higher level densities probably do not change the qualitative picture.³⁸ Also note that the quantity representing the functional errors is extensive and not practical to compare molecular densities.

Brorsen et al. presented a correspondence between the errors in the computed diatomic molecular densities near the bond critical point, and the errors in the computed molecular atomization energies for several semi-local and hybrid functionals (as well as one double hybrid).⁴¹ For some recent highly empirical hybrid functionals, the errors in densities and atomization energies were decoupled. Gould argued that the atomic test set of Medvedev et al.³⁴ is biased towards the high density limit, and their analysis based also on the gradients and Laplacians is biased towards the core regions.⁴² In addition to the densities, he also proposed testing the calculated left Fukui functions on a test set constituted of Li, C, and F atoms and found that a couple of functionals (*i.e.*, SOGGA11X,⁴³ TPSSh,⁴⁴ and B2PLYP⁴⁵) can be good both at densities and Fukui functions. Verma and Truhlar investigated the dipole moments of organic and inorganic compounds and found that density functionals describe better the charge distribution of single-reference systems than multi-reference systems.⁴⁶ In their analysis, the best performers were global hybrid functionals (*i.e.*, B97-1,²⁹ PBE0,³⁹ TPSSh,⁴⁴ and PW6B95⁴⁷) with relatively small fraction of exact exchange and a screened hybrid functional (*i.e.*, HSE06⁴⁸).

In this paper, we analyze several functionals from various rungs of the Jacob's ladder⁴⁹ of density functional approximations according to their density errors and density-driven exchange-correlation energy errors. In our modified methodology, we use composite coupled-cluster singles, doubles, triples, and quadruples (CCSDTQ) reference densities, and an intensive error measure. This way, our conclusions will be somewhat different even for the atomic density test set (B^{3+} , C^{4+} , N^{5+} , O^{6+} , F^{7+} , Ne^{8+} , Be , B^+ , C^{2+} , N^{3+} , O^{4+} , F^{5+} , Ne^{6+} , Ne) of Medvedev et al.³⁴ Furthermore, we construct another test set from small molecules (H_2 , LiH , Li_2 , LiF , BH_3 , H_2O , HF , CO , N_2 , F_2) with densities more relevant in chemistry. Additionally, we also discuss if there is a rationale behind the global hybrid or double hybrid functionals from the density's point of view. Since many parametrizations have been suggested in the literature for the PBE hybrid (PBEh)^{39,50,51} or PBE double hybrid (PBE-DH)^{52,53,54} functionals, we have studied the ratio of exact exchange and/or the ratio of second-order perturbative (PT2) correlation in these well-investigated forms.

Methodology and computational details

All the computations were performed with the MRCC quantum chemistry software.⁵⁵ To avoid any ambiguity, a close to infinite integration grid was used in the calculations: a 420-point Log3 radial grid (or a 415-point Log3 grid for hydrogen atoms),⁵⁶ and a 1202-point angular Lebedev grid.⁵⁷ For the calculations, the aug-cc-pVXZ⁵⁸ and aug-cc-pwCVXZ⁵⁹ ($X = D, T, Q, 5$) basis set families were applied. For the atomic density test set (B^{3+} , C^{4+} , N^{5+} , O^{6+} , F^{7+} , Ne^{8+} , Be , B^+ , C^{2+} , N^{3+} , O^{4+} , F^{5+} , Ne^{6+} , Ne) of Medvedev et al.,³⁴ we computed all-electron CCSD/aug-cc-pwCV5Z for the two-electron systems and

composite all-electron CCSDTQ/aug-cc-pwCV5Z densities otherwise. The latter is defined by eqs 2 and 3, where n_{basis}^{method} is the density evaluated with a particular method and basis set.

$$n_{aug-cc-pwCV5Z}^{comp.CCSDT} = n_{aug-cc-pwCV5Z}^{CCSD} + n_{aug-cc-pwCVQZ}^{CCSDT} - n_{aug-cc-pwCVQZ}^{CCSD} \quad (2)$$

$$n_{aug-cc-pwCV5Z}^{comp.CCSDTQ} = n_{aug-cc-pwCV5Z}^{comp.CCSDT} + n_{aug-cc-pwCVTZ}^{CCSDTQ} - n_{aug-cc-pwCVTZ}^{CCSDT} \quad (3)$$

For our new molecular density test set (H_2 , LiH, Li_2 , LiF, BH_3 , H_2O , HF, CO, N_2 , F_2), we computed CCSD/aug-cc-pV5Z density for the H_2 molecule and composite all-electron CCSDTQ/aug-cc-pwCV5Z densities [defined by eqs 2 and 3, but the effect of the quadruple excitations was considered with the aug-cc-pwCVTZ(-f) basis set] for the larger molecules. In our calculations, we used experimental molecular geometries taken from the NIST Computational Chemistry Comparison and Benchmark Database.⁶⁰

To represent the important rungs (semi-local and non-local) of the Jacob's ladder of density functional approximations, we selected five GGA (*i.e.*, SOGGA11,⁶¹ BLYP,^{17,23} BP86,^{17,18} PBE,²⁸ RGE2⁶²), five meta-GGA (*i.e.*, PKZB,⁶³ M06L,⁶⁴ SCAN,⁶⁵ MS0,⁶⁶ TPSS²⁷), five hybrid (*i.e.*, M062X,⁶⁷ SOGGA11X,⁴³ B3LYP,¹⁴ PBE0,³⁹ TPSSH⁴⁴), and five double hybrid (*i.e.*, B2PLYP,⁴⁵ B2GPPLYP,⁶⁸ PBE0-DH,⁵² PBE-QIDH,⁵³ PBE0-2⁵⁴) functionals with either physical or empirical construction. Additionally, we mapped the one- (a_X) and two-dimensional (a_X , a_C) parameter space in the PBEh (eq 4) and PBE-DH (eq 5) forms:

$$E_{XC}^{PBEh}[n] = a_X E_X^{exact}[n] + (1 - a_X) E_X^{PBE}[n] + E_C^{PBE}[n] \quad (4)$$

$$E_{XC}^{PBE-DH}[n] = a_X E_X^{exact}[n] + (1 - a_X) E_X^{PBE}[n] + a_C E_C^{PT2}[n] + (1 - a_C) E_C^{PBE}[n], \quad (5)$$

where E_X^{exact} is the exact exchange energy, E_X^{PBE} and E_C^{PBE} denote the PBE exchange and correlation energies, respectively, and E_C^{PT2} stands for the PT2 correlation energy.

To assess the performance of the various density functional approximations, we propose here a normed integral absolute deviation (NIAD) of the density functional (DF) and coupled-cluster (CC) densities and density derivatives ($p = n$ for the density, $p = |\nabla n|$ for its gradient, and $p = \nabla^2 n$ for its Laplacian) similar to the integral absolute deviation (IAD) applied earlier by Grabowski, Fabiano, et al. radially in spherical atoms and along the bond axis in diatomic molecules:²⁵

$$NIAD[p] = \frac{1}{N} \int |p_{DF}(\mathbf{r}) - p_{CC}(\mathbf{r})| d^3\mathbf{r} \xrightarrow{spherical} \frac{1}{N} \int |4\pi r^2 p_{DF}(r) - 4\pi r^2 p_{CC}(r)| dr, \quad (6)$$

where N is the number of electrons. This error measure is uniformly-distributed over all the electrons in space, which can be clearly demonstrated for spherically symmetric atoms, where the integration is over the radial density errors (for examples, see Figures S1-3 in the supporting information). In other words, the radial density near the nucleus is weighted equally to the radial density far from the nucleus. Another advantage of this error measure is that it can also be applied to non-spherical molecular systems. We chose the density errors per electron because we can directly compare this way the density errors for different atoms as opposed to the density errors per atom, which depends on the number of electrons in the atom. We retain this choice also for the molecules because we can compare the atomic and molecular density errors to each other, in contrast to the density errors per bond, which cannot be applied for atoms. In contrast to the suggestion of Gould⁴² that the inclusion of the gradient and Laplacian would bias the analysis towards the core regions, we also consider these quantities since the importance of the gradient and Laplacian can be supported by the universal formula for the exact Kohn-Sham potential of the two-electron spin-singlet systems (see eq 1). Moreover, the Laplacian may be particularly important in molecules as the Laplacian appears even at the bond critical point in the potential of the two-electron spin-singlet molecules like H_2 .

In thermochemical benchmarks, the calculated energies are usually said to be accurate if the errors in energy differences are lower than some threshold, for example, 1 kcal mol⁻¹. The choice of such absolute threshold is, however, not so convenient to assess whether the calculated densities are accurate or not. For this reason, we need to set up a relative scale for the magnitude of the errors. A natural choice

is to compare the errors in the semi-local or non-local density functional densities to the errors in the LDA (namely the SVWN5)^{69,22} densities. Note that the “average functional” as suggested by Medvedev et al.³⁴ depends on the functionals considered in the benchmark. Another natural choice would be the Hartree method with completely missing exchange and correlation. A further choice would be the HF method, but it is not a particularly suitable reference for density functional methods due to the fully exact treatment of the exchange and the completely missing electron correlation. Our test calculations show that comparing the errors to the LDA and Hartree density errors leads to the same ranking of the methods (see the Supporting Information).

For each descriptor p , we define the relative average normed error (RANE) as a dimensionless error measure.

$$RANE[p] = \frac{\sum_{system} NIAD_{system}^{method}[p]/\mathcal{N}_{sys}}{\sum_{system} NIAD_{system}^{LDA}[p]/\mathcal{N}_{sys}}, \quad (7)$$

where the sum runs over the systems of the test set, $NIAD_{system}^{method}$ is the NIAD defined by eq 6 calculated for the corresponding system with the given method, and \mathcal{N}_{sys} is the number of systems in the test set. The overall RANE is the average of the RANEs for the three descriptors.

In addition to the density errors, we show here the density-driven exchange-correlation energy errors per particle in the PBE exchange-correlation energy evaluated on the various approximate densities (for the sake of simplicity, we abbreviate this quantity as DDXC):

$$DDXC = \frac{E_{XC}^{PBE}[n_{DF}] - E_{XC}^{PBE}[n_{CC}]}{N}, \quad (8)$$

where n_{DF} and n_{CC} stand for the densities evaluated with the DF approximation and the reference CC method, respectively. Please do not confuse this quantity with the density-driven error defined by Kim et al. for total energies.³³ For a given test set, we show here the mean, mean absolute, and standard deviation DDXC. We assume that the DDXC does not depend much on the choice of the semi-local density functional approximation since the density-driven errors agree well in the non-empirical PBE and BLYP exchange-correlation energies (see Figure S4). These density-driven exchange-correlation energy errors also correlate with the ones in the semi-empirical SOGGA11 exchange-correlation energies, albeit the density-driven error in the SOGGA11 exchange-correlation energy significantly differs from the density-driven errors in the PBE or BLYP exchange-correlation energies on the SOGGA11 densities. This may indicate the opportunity for some internal error cancellation in this empirical method, but it does not follow directly from our results since we did not study here either the functional error (*i.e.*, the difference between the total energy obtained by evaluating the approximate functional at the exact electron density and exact total energy) or the density-driven total energy error.

Results and discussion

Our methodology in the analysis of the atomic (B^{3+} , C^{4+} , N^{5+} , O^{6+} , F^{7+} , Ne^{8+} , Be , B^+ , C^{2+} , N^{3+} , O^{4+} , F^{5+} , Ne^{6+} , Ne) density errors leads to somewhat different conclusions than those obtained by Medvedev et al.³⁴ In their analysis, the empirical M06L meta-GGA functional seemed to produce atomic densities similar to the LDA method. The PBE0 global hybrid GGA functional showed better performance on atomic densities than the TPSS meta-GGA and TPSSh global hybrid meta-GGA functionals. Contrarily, our comparison (Figure 1a) shows that the M06L functional produces clearly better atomic densities than the LDA method. The TPSS and TPSSh methods provide clearly better atomic densities than the PBE0 method. The observed differences can originate from several sources. (i) As an error measure, we apply here the normed (not size-extensive) integral absolute deviations instead of the size-extensive root mean square deviations on a radial grid. (ii) Our comparison relies on the average errors instead of the maximal errors (or on their combination). (iii) We normalize the errors to

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2 the LDA errors instead of the “average functional” errors. (iv) Our composite CCSDTQ reference
3 densities are more accurate for the many-electron systems than the CCSD reference densities.
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5 The average CCSD errors are small for the atomic test set (see Figure 1a), and thus using the
6 composite CCSDTQ densities as reference instead of the CCSD densities³⁴ does not lead to qualitative
7 changes (see also Figure S5). Normalization of the semi-local and non-local density functional errors to
8 the LDA errors does not significantly change the picture either (see Figure S5) compared to the
9 normalization to the “average functional” errors³⁴ because the improvements in the semi-local or non-
10 local density functional errors upon the LDA errors seem to be more or less simultaneous for the three
11 descriptors (see also Figure 1a). According to our analysis, the RANEs and the size extensive relative
12 average errors (RAEs), both relative to LDA, correlate relatively well (see Figure S5), although this can
13 be a minor source of the observed differences. For example, the different ranking of the TPSS and PBE0
14 methods comes from the application of an intensive error measure instead of an extensive one (*cf.* the
15 NIADs of these methods in Table S1). The overall relative maximum error (RME) is 1.34 for the TPSS
16 method, which originates from the density and the Ne system, as well as 1.12 for the PBE0 method,
17 which originates from the Laplacian and the Ne⁶⁺ system. While the overall relative maximum
18 normalized error (RMNE) is 0.95 for the TPSS method, which originates from the density and the Be
19 system, as well as 0.98 for the PBE0 method, which originates from the Laplacian and the Ne⁸⁺ system.
20 Considering the RANEs instead of the relative maximum normed errors (RMNEs), highly influences the
21 relative order of the methods (see Figure S5). Thus, using average errors instead of maximum ones seems
22 to be the major source of the observed differences. Notice that ranking the methods according to their
23 maximum errors would put too much weight on the Laplacian and on the highly-charged systems in the
24 comparison (see Figure S6). Considering either the RME or RMNE error measures, 9 methods out of 25
25 are judged by their Laplacian errors. Moreover, considering the RME error measure, 7 methods out of
26 25 are judged by the Laplacian errors on the Ne⁶⁺ system. While considering the RMNE error measure,
27 8 methods out of 25 are judged by the Laplacian errors on the Ne⁸⁺ system. On the other side, ranking
28 the methods according to their overall RANE errors puts equal weight on the density, gradient, and
29 Laplacian, as well as on the individual systems, even though a large part of the atomic test set (6 out of
30 14) includes two-electron systems.
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35 Since most of the semi-local and non-local density functionals simultaneously improve the atomic
36 densities, gradients, and Laplacians, the inclusion of the Laplacian in our comparison does not distort our
37 analysis much. The errors for the empirical SOGGA11, M06L, SOGGA11X, and M062X functionals
38 are higher in the Laplacians than in the densities or gradients; however, the overall errors are only
39 moderately larger than the errors in the densities and gradients. Contrarily, the RGE2 method gives
40 somewhat larger errors for the densities and smaller errors for the gradients and Laplacians than the
41 similar PBE method. Moreover, the HF method shows an uneven performance with quite erroneous
42 densities but with good gradients and Laplacians, although its overall performance for atomic densities
43 and density derivatives is similar to the best meta-GGA or hybrid functionals (*i.e.*, TPSS and TPSSh).
44 Interestingly, more exact exchange leads to more accurate density Laplacians (*cf.* BLYP, PBE, and TPSS
45 with their global hybrid versions: B3LYP, PBE0, and TPSSh), even though the exact exchange mixing
46 does not necessarily improve the densities if the semi-local part is reparametrized in the hybrid version
47 (*cf.* M06L and M062X). The correlation influences equally all the three density descriptors (*cf.* BLYP
48 and BP86). The B2GPPLYP double hybrid with 65% of exact exchange and 36% of PT2 correlation
49 provides better atomic densities than the B2PLYP double hybrid with 53% of exact exchange and 27%
50 of PT2 correlation. Similarly, the accuracy of the PBE-based double hybrid atomic densities increases
51 with the amount of exact exchange and PT2 correlation (PBE0-DH with 50% of exact exchange and
52 12.5% of PT2 correlation < PBE-QIDH with ~69% of exact exchange and ~33% of PT2 correlation <
53 PBE0-2 with ~79% of exact exchange and 50% of PT2 correlation). The PBE0-DH functional performs
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2 similar to the B2PLYP functional with similar exact exchange and PT2 correlation ratios. The PBE-
3 QIDH functional is somewhat better for atomic densities than the B2GPPLYP functional with similar
4 exact exchange and PT2 correlation ratios. Among the examined double hybrids, the PBE0-2 shows the
5 best accuracy. The Møller-Plesset second-order perturbation theory (MP2) method gives slightly better
6 atomic densities, but it performs worse than the CCSD method on the very compact cations because of
7 the poor description of the relatively large dynamic correlation in these systems. Concerning the densities
8 obtained with higher-order CC methods, the triple excitations have only a very small effect, while the
9 quadruple excitations have practically no contribution.

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11 For the molecular densities (H_2 , LiH, Li_2 , LiF, BH_3 , H_2O , HF, CO, N_2 , F_2), the average NIAD
12 density errors are somewhat larger than the corresponding average NIAD errors for atoms but the average
13 NIAD gradient and Laplacian errors are significantly smaller (see Tables S1 and S2). The overall (three-
14 descriptor) improvement in the NIAD errors is larger for the semi-local functionals than for the LDA
15 method. However, the relative order of the density functional methods only slightly changes (Figure 1b).
16 The SCAN meta-GGA functional performs better than the MS0 and TPSS functionals. The SOGGA11X
17 global hybrid functional provides better molecular densities than the B3LYP method. The PBE0-DH
18 global double hybrid functional is better than the B2PLYP method. The correlation becomes more
19 important in the many-electron molecules. This can be followed as the HF method tends to give worse
20 molecular densities, although its overall density errors are still comparable to the ones obtained with the
21 best GGA methods. The best double hybrid method (PBE0-2) yields similar molecular densities to the
22 MP2 method. The CCSD method works only slightly better for molecular densities. The CCSDT
23 densities are almost identical to CCSDTQ densities again. In contrast to the atomic density test set, there
24 is a stronger correlation between the average and maximum density errors, which shows that our
25 molecular density test set is well-balanced.

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27 For the different functionals, the density-driven error in the PBE (or other semi-local) exchange-
28 correlation energy does not always follow the same order we have previously observed for the density
29 errors (Figure 2a). One possible explanation is that the locally positive or negative errors in the exchange-
30 correlation energy per particle cancel each other in the exchange-correlation energy integral. Also notice
31 that the PBE exchange-correlation energy does not depend on the density Laplacian. For example, the
32 density-driven error in the PBE exchange-correlation energy for the atoms is significantly smaller on the
33 BP86 densities than on the RGE2 densities, where the overall density error is smaller only because of the
34 Laplacian (see Figure 1a). Similarly, the density-driven error in the PBE exchange-correlation energy is
35 smaller on the M06L densities than on the SCAN densities. The density-driven exchange-correlation
36 energy error is more systematic on the densities calculated with the best semi-local or non-local methods
37 than on the HF densities. As well as the MP2 atomic densities look only slightly better concerning the
38 density-driven exchange-correlation energy error than the best hybrid or double hybrid atomic densities.
39 (The correspondence between the atomic density errors and density-driven exchange-correlation energy
40 errors can be followed in Figure S7.)

41
42 For the molecules, the density-driven errors in the PBE exchange-correlation energy (Figure 2b)
43 are generally smaller than the errors we have observed for atoms. The meta-GGA densities lead to smaller
44 density-driven exchange-correlation energy errors than the GGA densities (*cf.* PBE with TPSS). This
45 difference also remains among the hybrid functionals, where the density-driven exchange-correlation
46 energy error is smaller on the global hybrid meta-GGA densities than on the global hybrid GGA densities
47 (*cf.* PBE0 with TPSSh). The molecular densities obtained by the best semi-local or non-local density
48 functionals are better again than the molecular HF densities according to their density-driven exchange-
49 correlation energy errors. Furthermore, the density-driven error in the PBE exchange-correlation energy
50 is slightly smaller on the PBE0-2 densities than on the MP2 densities. Considering both the molecular
51 density errors and density-driven errors in the semi-local exchange-correlation energies (see Figure S8),
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1
2 the best performers among their kind in the order of increasing accuracy are the PBE GGA functional,
3 the TPSS and SCAN meta-GGA functionals, the TPSSh hybrid functional, and the PBE0-2 double hybrid
4 functional. Notice that all these methods have non-empirical origin, which supports the main conclusion
5 of Medvedev et al.³⁴
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7 Seeking for an optimal exact exchange mixing in the PBE hybrid form, we changed (from 0% to
8 100% by 5%) the ratio of exact exchange. On the atomic densities, the optimal exact exchange mixing
9 ratios were found at ~40% for the density, at ~80% for the gradient, at ~85% for the Laplacian, and at
10 ~80% for the three descriptors since the error in the Laplacian of the density is very sensitive to the ratio
11 of exact exchange (Figure 3a). However, such high fraction of exact exchange only seems to be optimal
12 because the very compact two- and four-electron systems are overrepresented in the test set. Note that
13 for the neon atom, which has a chemically more relevant electronic structure, the lowest absolute errors
14 can be obtained at ~35% of exact exchange for the density and the gradient, at ~75% for the Laplacian,
15 and at ~35% for the three descriptors. Similarly, for molecules, we have found the minimal mean absolute
16 error at ~35% of exact exchange for the density and gradient, at ~65% for the Laplacian, and at ~45%
17 for the three descriptors (Figure 3b).
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20 For the atoms, the mean absolute DDXC in the PBE exchange-correlation energy is the lowest at
21 high ratios of exact exchange (90%), although this error is the most systematic at ~25% of exact exchange
22 mixing in the PBEh form (Figure 4a). The preference towards the full exact exchange originates again
23 from the overrepresented very compact systems in the test set. For the neon atom, the mean absolute
24 DDXC in the PBE exchange-correlation energy is the lowest at ~40% of exact exchange mixing. For the
25 molecules, the minimal density-driven exchange-correlation energy error appears at ~40% as well, where
26 the errors are also quite systematic (Figure 4b). At this ratio of exact exchange, the density-driven error
27 in the PBE exchange-correlation energy is significantly lower on the PBEh densities than on the HF
28 densities. Considering both the overall (three-descriptor) density error and the density-driven error in the
29 PBE (or other semi-local) exchange-correlation energy, a fair compromise might be made around 40%
30 of exact exchange mixing in the PBEh form for the chemically relevant densities (*e.g.*, the neon atom or
31 the molecules considered here). Notice that this is close to the global hybrid PBE38 method.⁵¹
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34 Also seeking for an optimal PT2 correlation mixing in the PBE double hybrid form, we varied
35 the ratio of PT2 correlation (from 0% to 100% by 5%) at several ratios of exact exchange. Regarding the
36 densities of the very compact atomic systems, the MP2 method seems to be the global minimum in the
37 two-dimensional parameter space (Figure 5a). Interestingly, the PT2 correlation mixing corresponding
38 to the one-dimensional minimum for a fixed 80% of exact exchange shifts to ~55% for the molecular
39 densities (Figure 5b). The global optimum seems to be around 95% of exact exchange and 80% of PT2
40 correlation.
41

42 For the very compressed atomic systems, the lowest density-driven error in the PBE exchange-
43 correlation energy seems to be around the MP2 method again (Figure 6a). For a fixed 80% of exact
44 exchange, a minimum appears at 55% of PT2 correlation mixing in the one-dimensional parameter space.
45 For the molecules, the global minimum of the density-driven exchange-correlation energy error seems
46 to be at 90% of exact exchange and 70% of PT2 correlation (Figure 6b). For a fixed 80% of exact
47 exchange mixing, there is a minimum in the one-dimensional parameter space at ~55% of PT2
48 correlation. The PT2 correlation ratio corresponding to the minimum for a fixed exact exchange ratio
49 increases nearly linearly with the ratio of the exact exchange. Considering both the overall (three-
50 descriptor) density errors and the density-driven errors in the PBE (or other semi-local) exchange-
51 correlation energy, the global optimum seems to be at 90-95% of exact exchange and 70-80% of PT2
52 correlation. Furthermore, there is a one-dimensional minimum for a fixed 80% of exact exchange at
53 ~55% of PT2 correlation for the examined molecules (with not too compact densities). Notice that the
54 PBE-DH method with these mixing factors is not so far from the PBE0-2 method.
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Conclusions

According to the core theorem of density functional theory, the electron density, similar to the many-body wave function, contains all the information about the examined system. This property enables the error in the computed electron density to measure the proximity of a given density functional approximation to the exact functional. In the development of density functional approximations, it was assumed that the electron density improves together with the energetics. Recently, Medvedev et al.³⁴ have argued that some modern density functional approximations with many empirical parameters and a very flexible functional form started producing worse electron densities despite their improved accuracy on energetics.

In this paper, we have assessed the performance of several density functional methods from various rungs of the Jacob's ladder of the density functional approximations. Our analysis uses a different methodology for the calculation of the density errors, in which the quantity measuring the accuracy of various methods is based on their average performance and is not size-extensive. Moreover, it can directly be applied to the comparison of non-centrosymmetric molecular densities. We have also constructed a small molecular test set. Notice that in the atomic test set of Medvedev et al.,³⁴ the chemically less relevant very compact atomic electron densities are overrepresented. Although their main message still holds, using an intensive error measure instead of an extensive one, aggregating the errors for different systems and descriptors by averaging instead of taking the maximum values, and applying a more balanced molecular test set lead to somewhat different conclusions about the performance of certain density functional approximations. For example, the meta-GGA level TPSS functional produces clearly better densities than the global hybrid PBE0 functional, and the empirically constructed M06L functional gives clearly better densities than the LDA method. We have also shown that better densities can be obtained with particular global double hybrid methods. For instance, the PBE0-2 double hybrid approaches the accuracy of the MP2 method for atomic densities and outperforms it for molecular ones.

In this work, we have also compared the density functional approximations with respect to the density-driven error in the semi-local exchange-correlation energy. According to our results, the density-driven exchange-correlation energy errors do not always follow the same order that has been previously observed for the density errors. This is partially because the semi-local exchange-correlation energy functional we have used to indicate the density-driven exchange-correlation energy errors does not depend explicitly on the density Laplacian. Furthermore, the density-driven error in the semi-local exchange-correlation energy can occasionally integrate to almost zero. The density-driven exchange-correlation energy errors are smaller on meta-GGA densities than on GGA densities. The quality of the parent semi-local functional also greatly influences the density-driven exchange-correlation energy errors on the global hybrid or double hybrid densities. The density-driven errors in the semi-local exchange-correlation energies are much smaller on the densities calculated with the best semi-local or non-local density functionals than on the HF densities. This tendency significantly intensifies on molecular densities.

Considering both the density errors and the density-driven errors in the semi-local exchange-correlation energies, the best performers among their kind in the order of increasing accuracy are the PBE, the TPSS or SCAN, the TPSSh, and the PBE0-2 methods, all with non-empirical origin. In the PBE global hybrid form, a fair compromise can be made at ~40% of exact exchange mixing, which is close to the PBE38 method. In the studied range, the global optimum in the PBE global double hybrid form appears at 90-95% of exact exchange and 70-80% of PT2 correlation, even though a one-dimensional minimum has been found for a fixed 80% of exact exchange at 55% of PT2 correlation mixing, which is not so far from the successful PBE0-2 global double hybrid method. Finally, we believe that our methodology can help developing more reliable hybrid or double hybrid functionals that approach more

1
2 the exact functional than the ones fitted to chemical energetics.
3

4 **Additional information**

5 We make the computed molecular reference densities available at
6 <https://drive.google.com/open?id=0B4I8Qk8TWhVvS0xYVFN3OGxIaEU>.
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9 **Acknowledgments**

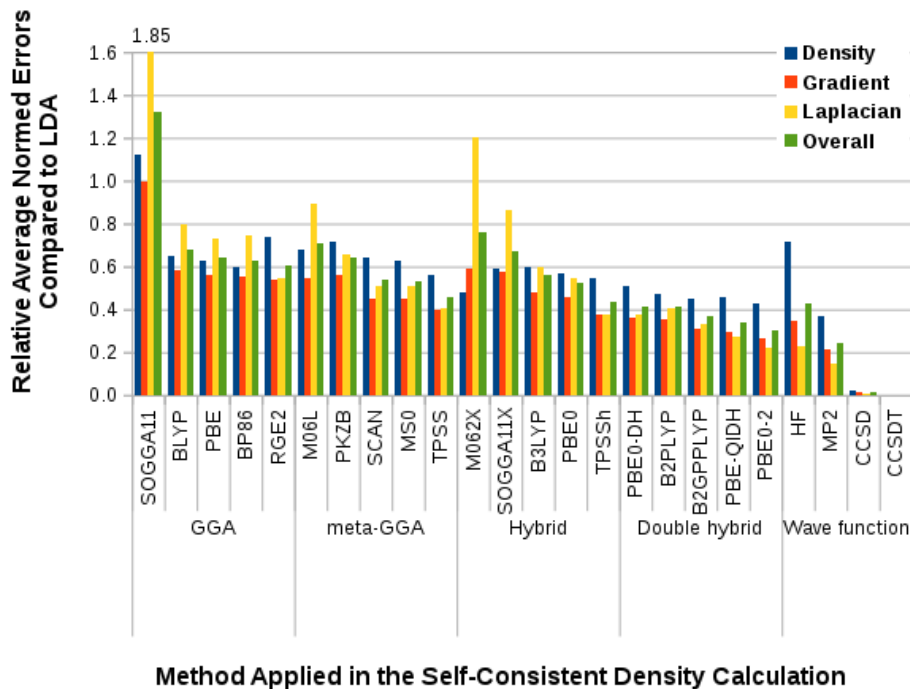
10 The authors thank the Hungarian National Higher Education and Research Network (NIIF) for
11 the computer time.
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14 **Supporting information**

15 The computed atomic densities, further information about the density errors and density-driven
16 exchange-correlation energy errors, as well as detailed results for the discussed methods. This
17 information is available free of charge via the Internet at <http://pubs.acs.org/>.
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Figures

a)



b)

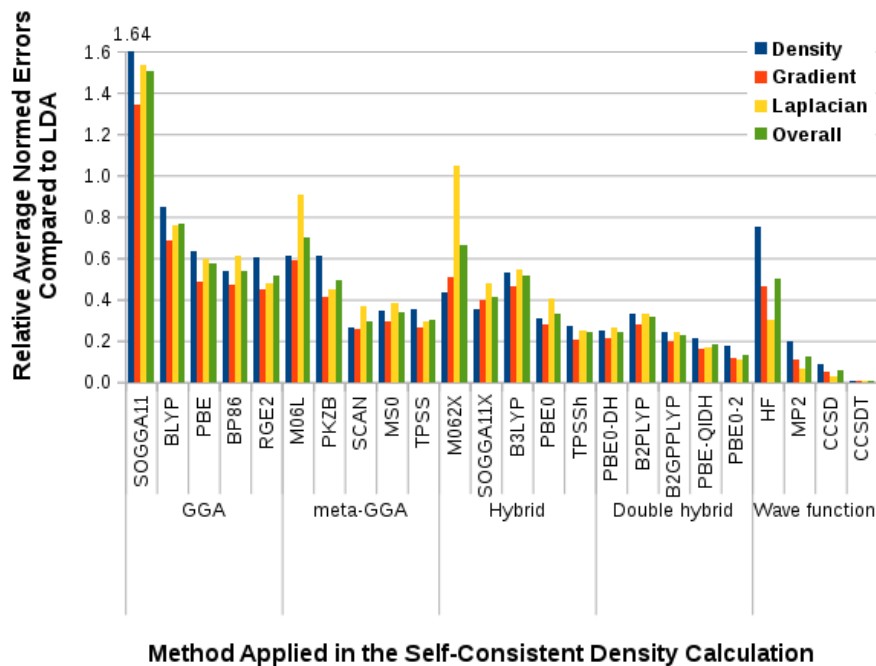
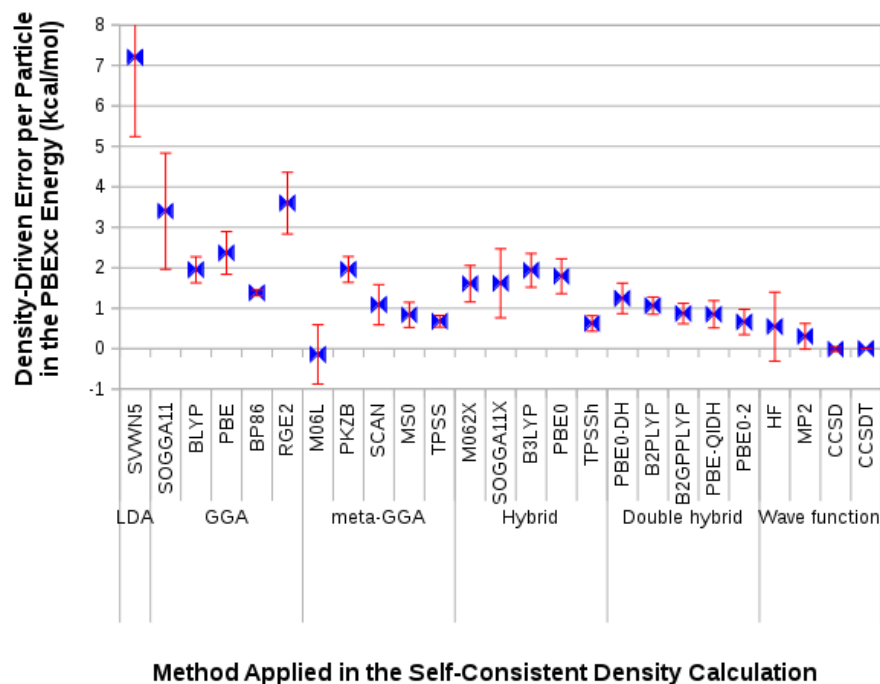


Figure 1 Relative average normed errors (RANE) for the atoms (a) and molecules (b) calculated with various methods compared to the local density approximation (LDA)

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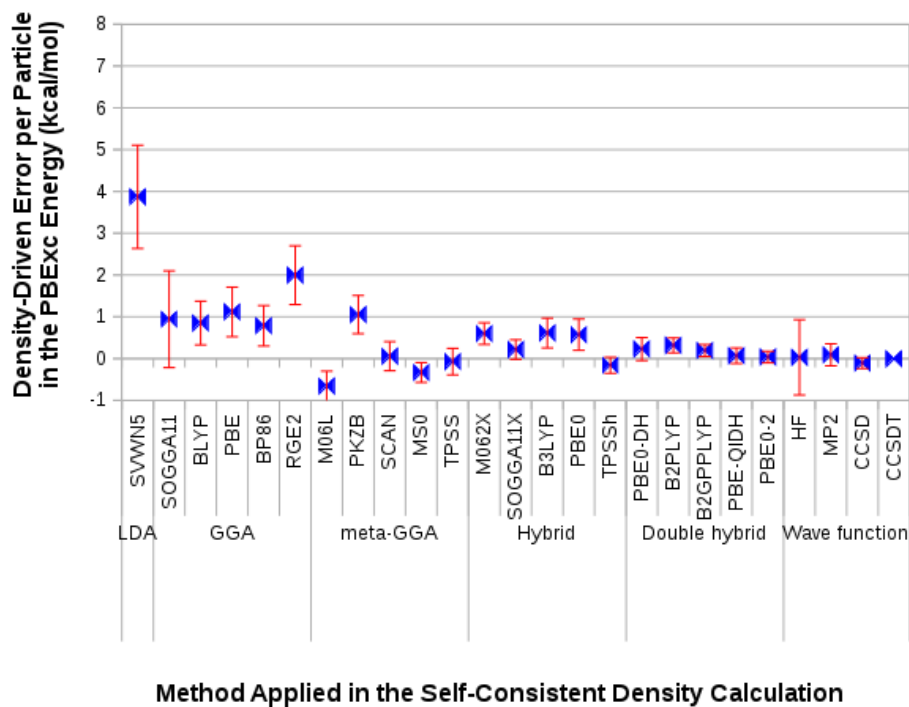
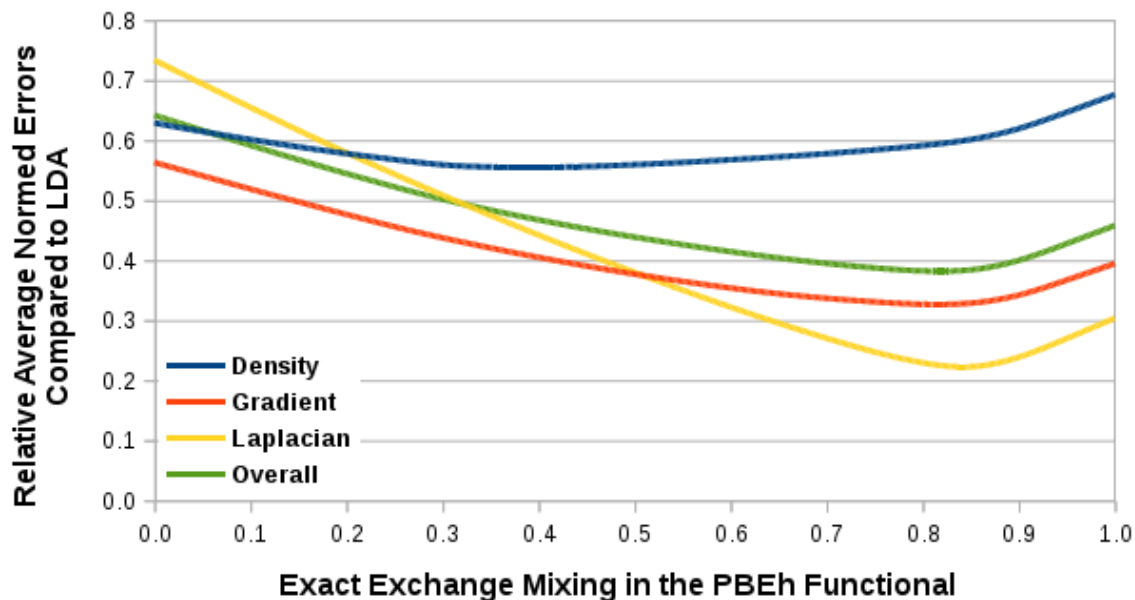


Figure 2 Density-driven error per particle in the PBE exchange-correlation energy (DDXC) evaluated on densities calculated with various methods for the atomic (a) and molecular (b) test sets. (The error bars show the standard deviation for the errors.)

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b)

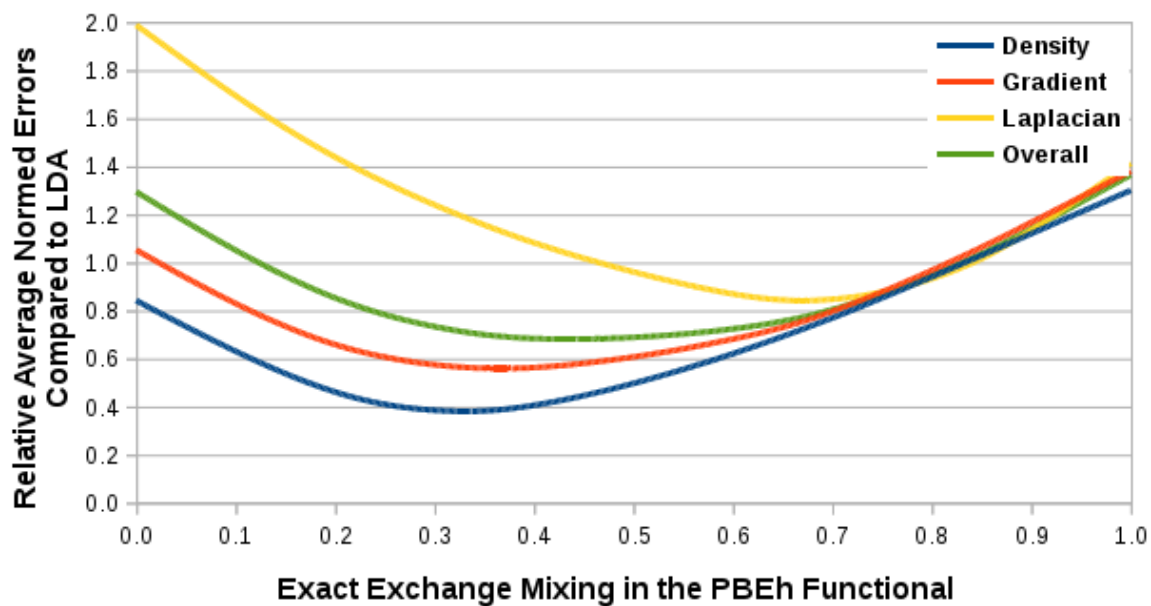
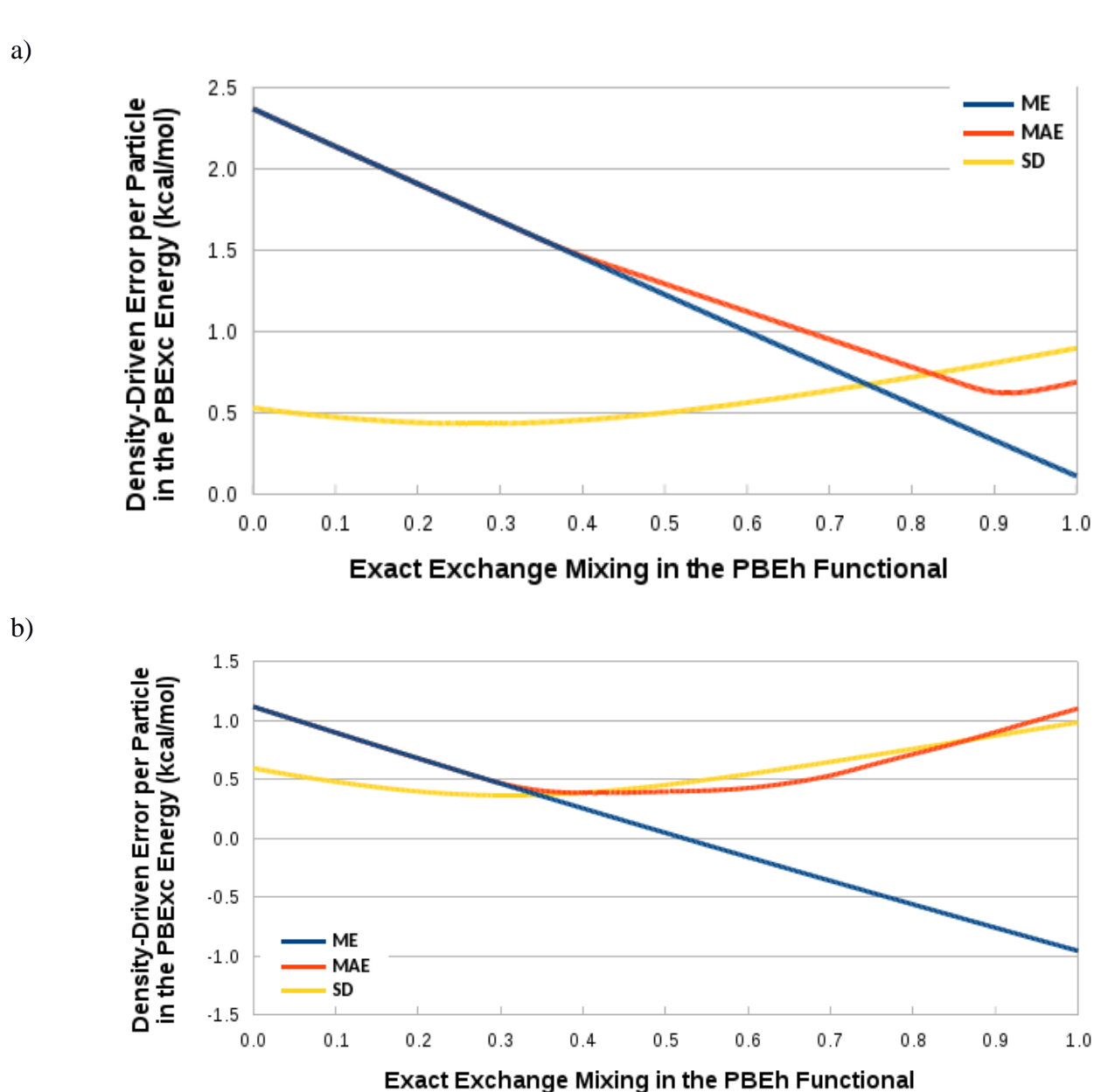


Figure 3 Dependence of the relative average normed errors (RANE) for the atoms (a) and molecules (b) on the exact exchange mixing in the PBEh functional compared to the local density approximation (LDA)



42 **Figure 4** Dependence of the density-driven error per particle in the PBE exchange-correlation energy
43 (DDXC) of the atoms (a) and molecules (b) on the exact exchange mixing in the PBEh densities (ME:
44 mean error; MAE: mean absolute error; SD: standard deviation of the errors)
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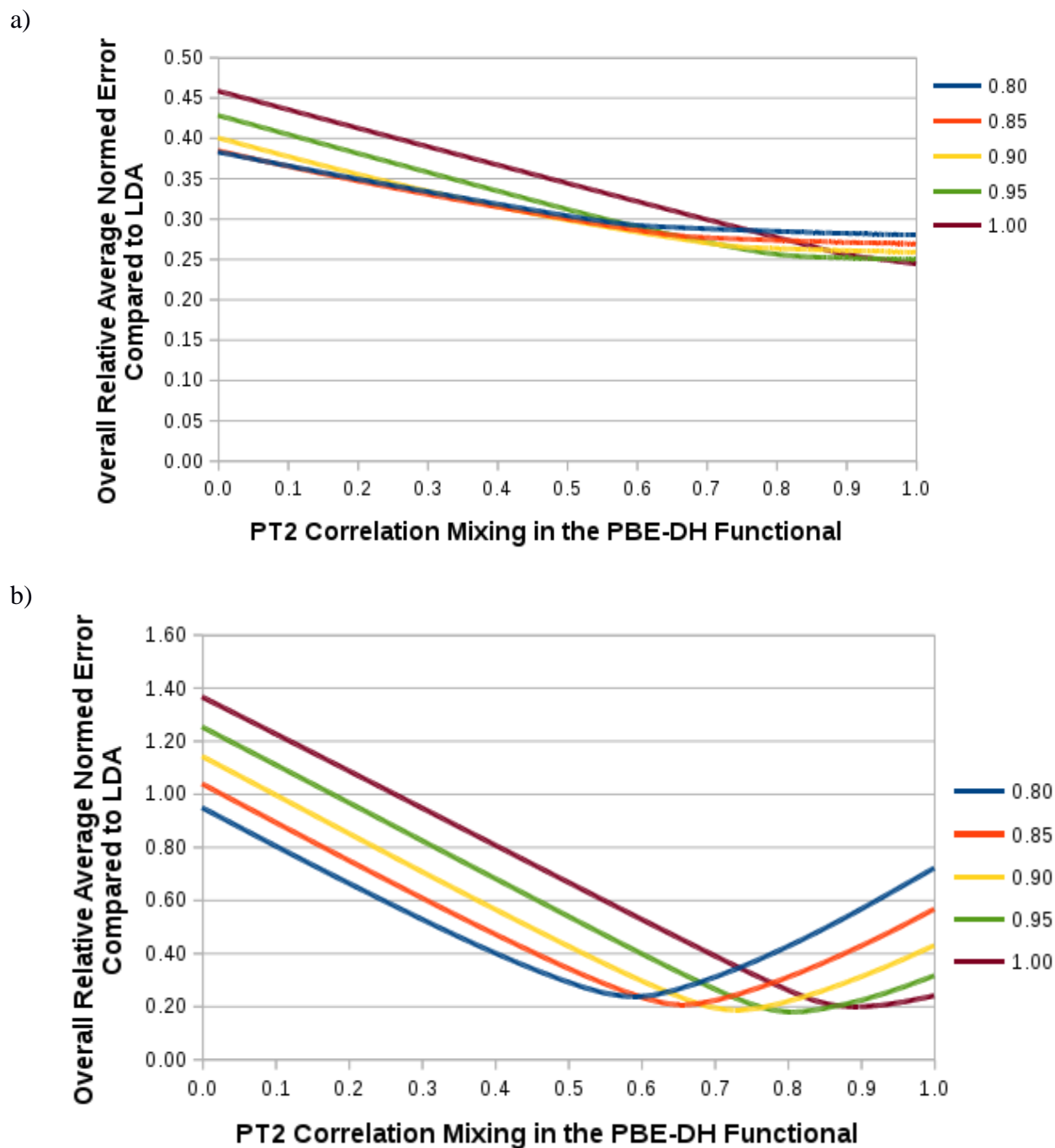


Figure 5 Dependence of the overall (three-descriptor) relative average normed error (RANE) on the second-order perturbative correlation mixing in the PBE-DH functional relative to the local density approximation for various exact exchange mixing ratios (displayed in the key) for the atomic (a) and molecular (b) test sets

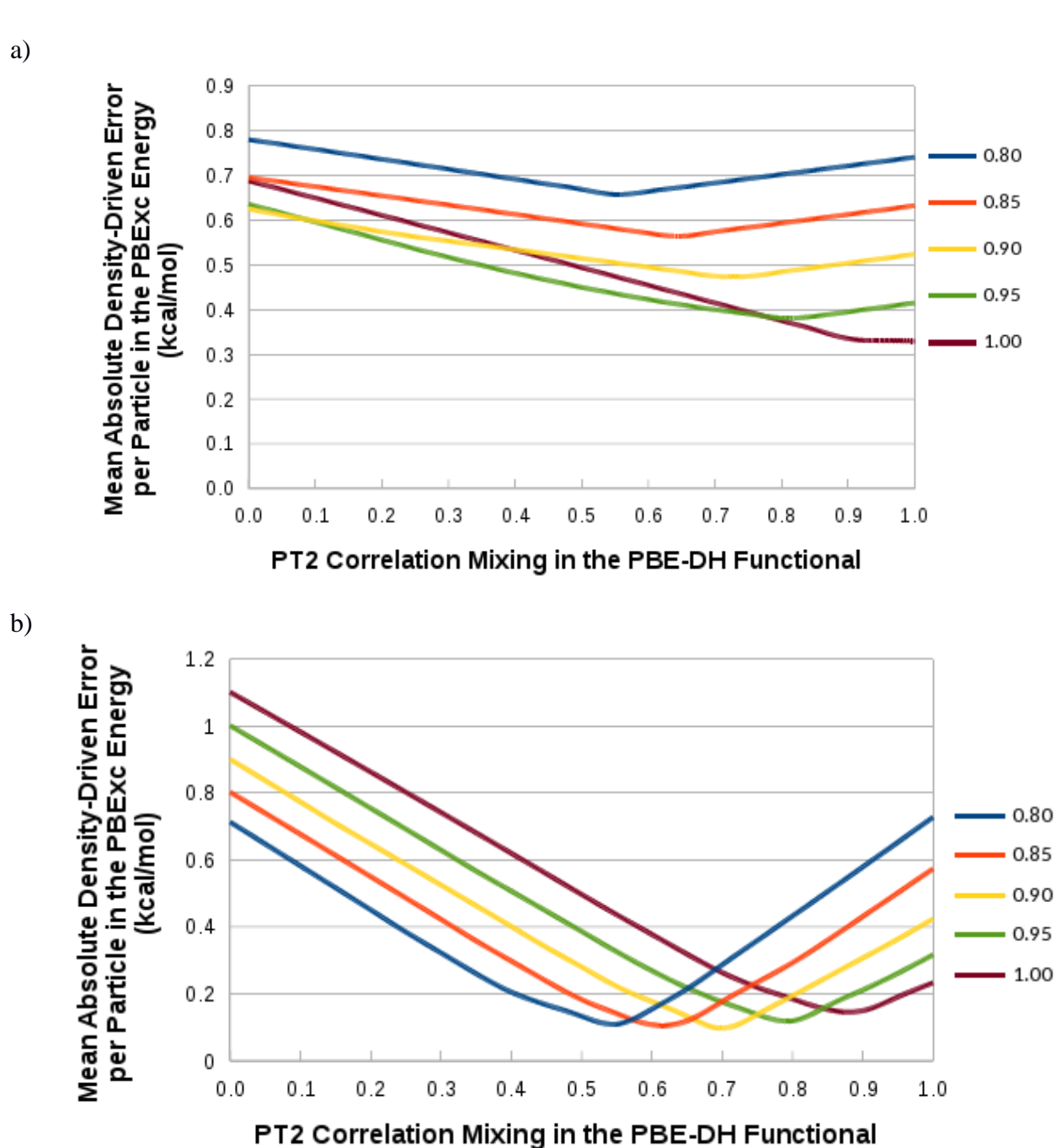


Figure 6 Dependence of the density-driven error per particle in the PBE exchange-correlation energy (DDXC) of the atoms (a) and molecules (b) on the second-order perturbative correlation mixing in the PBE-DH densities for various exact exchange mixing ratios (displayed in the key)

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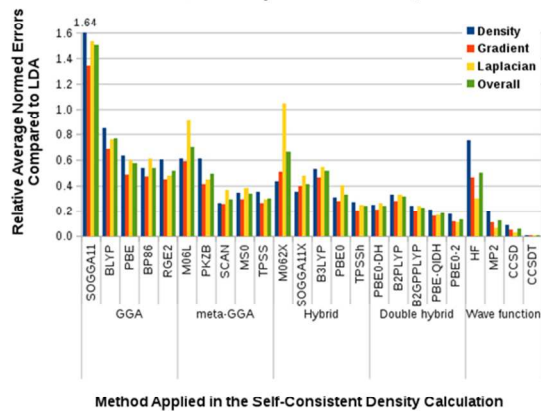
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Molecules



Reference: composite CCSDTQ densities



Density Errors

$$\frac{1}{N} \int |n_{DF}(r) - n_{CC}(r)| d^3r$$

Gradient Errors

$$\frac{1}{N} \int ||\nabla n_{DF}(r) - |\nabla n_{CC}(r)|| d^3r$$

Laplacian Errors

$$\frac{1}{N} \int |\nabla^2 n_{DF}(r) - \nabla^2 n_{CC}(r)| d^3r$$

Method Applied in the Self-Consistent Density Calculation

TOC graphic

85x47mm (300 x 300 DPI)