

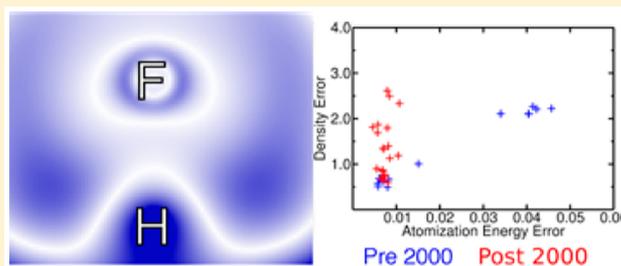
# Is the Accuracy of Density Functional Theory for Atomization Energies and Densities in Bonding Regions Correlated?

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## S Supporting Information

**ABSTRACT:** The development of approximate exchange–correlation functionals is critical for modern density functional theory. A recent analysis of atomic systems suggested that some modern functionals are straying from the path toward the exact functional because electron densities are becoming less accurate while energies are becoming more accurate since the year 2000. To investigate this trend for more chemically relevant systems, the electron densities in the bonding regions and the atomization energies are analyzed for a series of diatomic molecules with 90 different functionals. For hybrid generalized gradient approximation functionals developed since the year 2000, the errors in densities and atomization energies are decoupled; the accuracy of the energies remains relatively consistent while the accuracy of the densities varies significantly. Such decoupling is not observed for generalized gradient and meta-generalized gradient approximation functionals. Analysis of electron densities in bonding regions is found to be important for the evaluation of functionals for chemical systems.



Density functional theory (DFT) is one of the most commonly used methods in quantum chemistry.<sup>1–3</sup> A DFT calculation in the Kohn–Sham framework<sup>4</sup> with the exact exchange–correlation (XC) functional would give the exact density and energy of the system, but as this functional is unknown, approximations to the exact functional are necessary. Both physically motivated<sup>5</sup> and empirically motivated<sup>5–7</sup> approaches have emerged for approximating the XC functional. The latter approach has dominated recent functional development, with some recent functionals containing over 50 empirical parameters.<sup>8</sup> Functional development has typically focused on improving the energy,<sup>9–11</sup> rather than the density, implicitly assuming that if a functional gives a better energy, the density will likewise be improved. Exceptions to this focus include the B97-2<sup>12</sup> functional and the HCTH<sup>13–15</sup> family of functionals, which were constructed by attempting in part to reproduce the exact density of a test set of molecules. Additionally, other studies have examined the density produced by a limited number of DFT functionals.<sup>16–19</sup> A recent provocative investigation<sup>20,21</sup> questioned whether recent functional development is straying from the path of finding the exact functional. This study examined the densities of different functionals for a series of neutral and charged atoms using coupled cluster singles and doubles (CCSD) densities as a reference. For those atoms, the XC functionals were found to give better densities chronologically until the early 2000s, after which the errors in the density tended to increase chronologically with the increasing prevalence of empirical fitting. The study therefore concluded that recent functional development has strayed from the path of better approximations to the exact functional.

Although this study<sup>20</sup> is intriguing, it does not provide information about how the various functionals perform for systems with chemical bonds, which are of interest to computational chemists.<sup>22</sup> The modern functionals could potentially provide accurate densities in the chemically relevant bonding regions of molecules, resulting in the more accurate energies associated with these functionals. Additionally, many of the atoms in the recent study had a large positive charge, leading to densities that are highly localized in the core region and thus are dissimilar to chemically relevant systems. The accurate molecular energies reported for many of the modern functionals could be due to these functionals predicting correct densities in the bonding regions with the errors of the densities in the core regions canceling out, as the densities in the core regions remain nearly constant upon chemical bonding. Furthermore, this previous study compares the errors in the densities of these atomic systems to the errors in the energies of a test set of molecules obtained from a different study,<sup>23</sup> preventing a consistent comparison. The present study compares the electron densities in the chemically relevant bonding regions and the atomization energies for a series of diatomic molecules computed with 90 different density functionals to CCSD reference calculations.

We performed DFT calculations on a test set of 14 closed-shell diatomic molecules and their constituent atoms using 90 different DFT functionals. A complete list of the functionals is

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provided in the [Supporting Information](#). The 14 closed-shell diatomic molecules examined in this study were Cl<sub>2</sub>, CO, F<sub>2</sub>, FCl, HF, Li<sub>2</sub>, LiF, LiH, N<sub>2</sub>, Na<sub>2</sub>, P<sub>2</sub>, SC, Si<sub>2</sub>, and SiO with bond lengths obtained from the G2/97 test set, as given in Table S2 of the [Supporting Information](#),<sup>24</sup> and not optimized for each level of theory. To ensure that the calculations were converged with respect to basis set and DFT integration grids, a large basis set with tight and diffuse functions, aug-cc-pCVQZ,<sup>25</sup> was used, and fine integration grids were used for calculating the XC potential.

For each molecule and functional, a one-dimensional slice of the density was calculated on a grid along two directions with a grid spacing of 0.01 Å. While the previous study<sup>20</sup> used a combination of the density, the gradient of the density, and the Laplacian of the density to compute a measure referred to as the “normalized error,” the present study focuses on only the density, as all functional types use the density as input. The first direction, denoted the on-axis density, is the density on the line connecting the two nuclei of the diatomic molecule. As the density in the core region is much higher than that in the valence region, and this study focuses on the density in the chemically relevant bonding region of the molecule, the on-axis bonding density was characterized in terms of the density points with the smallest values. Specifically, using the CCSD density values as a metric, the lowest 15% of the on-axis grid points were included in this analysis, resulting in a total of  $N_{\text{on}}$  points in the vicinity of the chemical bond. The root-mean-square deviation (RMSD) of the on-axis density for each functional and molecule was then calculated relative to the CCSD density as

$$\text{RMSD}_{\text{on,functional,molecule}} = \sqrt{\frac{1}{N_{\text{on}}} \sum_i^{N_{\text{on}}} (\rho_i^{\text{CCSD,molecule}} - \rho_i^{\text{functional,molecule}})^2} \quad (1)$$

For each functional, an average of the on-axis RMSD across all of the diatomic molecules in this study was calculated to determine the on-axis RMSD of each functional, denoted  $\text{RMSD}_{\text{on,functional}}$ . The average RMSD is presented rather than focusing on both the average and maximum RMSD because the average performance of a functional is expected to be more meaningful than the worst-case performance.

The second direction on which the density was calculated, denoted the off-axis density, is the density on a 5.0 Å line segment perpendicular to the on-axis density with the midpoint of this line segment passing through the minimum of the CCSD on-axis density of each molecule. The large distance of 5.0 Å was chosen to ensure that the density was virtually zero at the end points of the perpendicular line segment, which was discretized into  $N_{\text{off}}$  grid points. As each diatomic molecule has cylindrical symmetry, this off-axis density does not depend on the specific perpendicular axis chosen. To account for this cylindrical symmetry, the off-axis RMSD relative to the CCSD density for each molecule and functional is weighted by  $\pi r_i$ , where  $r_i$  is the distance of the grid point from the midpoint of the axis:

$$\text{RMSD}_{\text{off,functional,molecule}} = \sqrt{\frac{1}{N_{\text{off}}} \sum_i^{N_{\text{off}}} \pi r_i (\rho_i^{\text{CCSD,molecule}} - \rho_i^{\text{functional,molecule}})^2} \quad (2)$$

For each functional, an average of the off-axis RMSD across all of the diatomic molecules in this study was calculated to determine the off-axis RMSD of each functional, denoted  $\text{RMSD}_{\text{off,functional}}$ .

A single measure of the accuracy of the density of each functional was obtained by a procedure similar to that of the recent study on atoms, whereby the on-axis and off-axis density deviations were divided by the median on-axis and off-axis density deviation among the 90 functionals, respectively. The two resulting scaled deviations were then added together to compute the density error for each functional:

$$\text{Density\_Error}_{\text{functional}} = \frac{\text{RMSD}_{\text{off,functional}}}{\text{median}\{\text{RMSD}_{\text{off,functionals}}\}} + \frac{\text{RMSD}_{\text{on,functional}}}{\text{median}\{\text{RMSD}_{\text{on,functionals}}\}} \quad (3)$$

where  $\{\text{RMSD}_{\text{on/off,functionals}}\}$  is the set of all  $\text{RMSD}_{\text{on/off,functional}}$  values. The mean absolute atomization energy error (MAAEE) for each functional was computed using the CCSD reference values as

$$\text{MAAEE}_{\text{functional}} = \frac{1}{N_{\text{mol}}} \sum_j^{N_{\text{mol}}} \left| E_{\text{atomization}_j}^{\text{CCSD}} - E_{\text{atomization}_j}^{\text{functional}} \right| \quad (4)$$

where  $E_{\text{atomization}_j}^{\text{functional}}$  is the atomization energy of molecule  $j$  using the specified functional, and  $N_{\text{mol}}$  is the number of molecules. Note that CCSD reference values were used for both the densities and the MAAEEs to maintain consistency, although CCSD(T) would be more quantitatively accurate. Additional technical details about the calculations are provided in [Computational Methods](#).

The functionals with the 20 smallest and largest density errors in the chemical bonding region are presented in [Tables 1 and 2](#), respectively. The functional types are local density approximation (LDA), generalized gradient approximation (GGA), meta-GGA (mGGA), hybrid-GGA (hGGA), and double-hybrid-GGA (dhGGA). In this analysis, hGGA broadly includes all hybrid functionals that could also be of LDA or mGGA type and includes M06-L, which is not strictly a hybrid functional. A graph of the density error versus the year of development for all 90 functionals is presented in [Figure 1](#). A table of the density errors and MAAEEs, as well as a list of references for all functionals in this study, are provided in the [Supporting Information](#).

[Table 1](#), which enumerates the most accurate functionals in terms of density, is dominated by functionals of hGGA type, as expected because functionals of hGGA type are on the fourth rung of “Jacob’s ladder” of DFT.<sup>26</sup> The single dhGGA functional, which is on the fifth rung, used in this study also appears on the list of most accurate density functionals. This trend indicates that functionals on higher rungs of Jacob’s ladder are capable of predicting better densities than functionals on lower rungs of Jacob’s ladder. The list of least accurate functionals in terms of density is more varied, with contributions from all four lowest rungs of Jacob’s ladder, indicating that higher rungs of Jacob’s ladder can still predict poor densities. [Figure 1](#) shows a slight upward trend in the density error beginning in the early 2000s. In contrast, [Figure 2](#) illustrates that the MAAEE exhibits a clear downward trend over all years. These two graphs suggest that functional

**Table 1. Functional; Year of Development; Functional Type; Density Error, As Defined in eq 3; and Mean Absolute Atomization Energy Error (MAAEE), As Defined in eq 4, for the 20 Functionals with Smallest Density Errors**

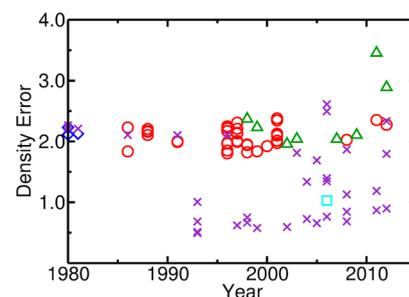
functional	year	type	density error	MAAEE
B3P86	1993	hGGA	0.494	0.0080
B3PW91	1993	hGGA	0.512	0.0058
PBE0	1999	hGGA	0.577	0.0058
$\tau$ HCTHhyb	2002	hGGA	0.594	0.0081
B97	1997	hGGA	0.621	0.0071
B97-3	2005	hGGA	0.657	0.0070
B97-1	1998	hGGA	0.666	0.0082
B3LYP	1993	hGGA	0.683	0.0061
B3LYPV3	1993	hGGA	0.683	0.0061
B3LYPV1R	1993	hGGA	0.684	0.0067
X3LYP	2008	hGGA	0.686	0.0065
CAMB3LYP	2004	hGGA	0.726	0.0074
B98	1998	hGGA	0.750	0.0067
M06-2X	2006	hGGA	0.763	0.0074
$\omega$ B97X	2008	hGGA	0.845	0.0085
SOGGA11X	2011	hGGA	0.868	0.0068
APFD	2012	hGGA	0.897	0.0055
BHHLYP	1993	hGGA	1.006	0.0151
B2PLYP	2006	dhGGA	1.029	0.0298
$\omega$ B97	2008	hGGA	1.127	0.0085

**Table 2. Functional; Year of Development; Functional Type; Density Error, As Defined in eq 3; and Mean Absolute Atomization Energy Error (MAAEE), As Defined in eq 4, for the 20 Functionals with Largest Density Errors**

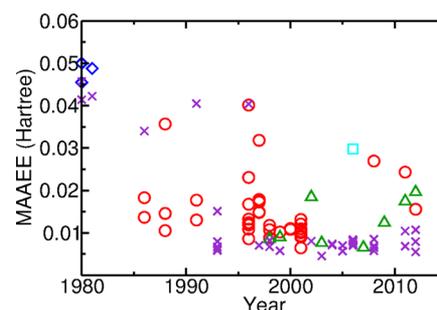
functional	year	type	density error	MAAEE
M11-L	2011	mGGA	3.455	0.0175
MN12-L	2012	mGGA	2.889	0.0196
M06-L	2006	hGGA	2.612	0.0079
M06-HF	2006	hGGA	2.496	0.0084
OPBE	2001	GGA	2.379	0.0103
VS98	1998	mGGA	2.370	0.0085
SOGGA11	2011	GGA	2.352	0.0068
OPW91	2001	GGA	2.346	0.0100
MN12SX	2012	hGGA	2.335	0.0107
PBEX	1997	GGA	2.308	0.0318
N12	2012	GGA	2.273	0.0156
VWN1RPA	1980	hGGA	2.265	0.0414
GILL	1996	GGA	2.248	0.0401
GVWN1RPA	1996	GGA	2.234	0.0120
PKZB	1999	mGGA	2.231	0.0090
SVWN	1980	LDA	2.231	0.0455
OP86	1986	GGA	2.230	0.0137
VWN5	1980	hGGA	2.223	0.0457
GVWN	1996	GGA	2.220	0.0086
GPZ81	1996	GGA	2.215	0.0109

development has improved the predictions of energy without a corresponding improvement in the prediction of the density. This trend is clarified by Figure 3, which plots the density error versus the MAAEE on the same graph.

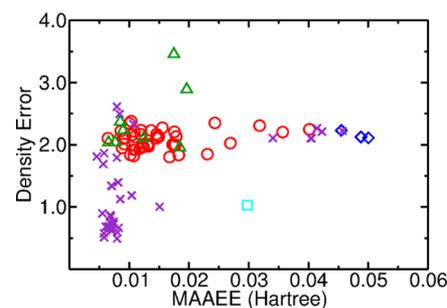
For the analysis of Figure 3, it is useful to investigate the correlation of the density error and atomization energy error within a given functional type. For functionals of LDA type (blue diamonds) and dhGGA type (cyan square), the data are not sufficient to draw any conclusion. All the LDA functionals are tightly clustered, mainly because LDA functionals differ



**Figure 1.** Plot of density error, as given in eq 3, versus year of functional development for the 90 functionals in this study. Blue diamonds, red circles, green triangles, purple X's, and the cyan square represent functionals of LDA, GGA, mGGA, hGGA, and dhGGA type, respectively.



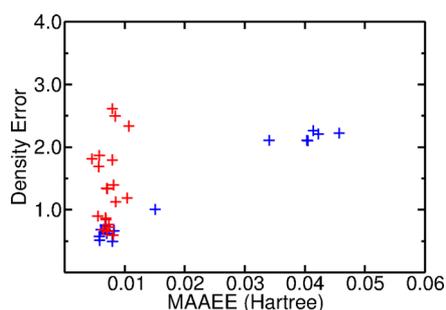
**Figure 2.** Plot of mean absolute atomization energy error, as given in eq 4, versus year of functional development for the 90 functionals in this study. Blue diamonds, red circles, green triangles, purple X's, and the cyan square represent functionals of LDA, GGA, mGGA, hGGA, and dhGGA type, respectively.



**Figure 3.** Plot of density error versus mean absolute atomization energy error for the 90 functionals in this study. Blue diamonds, red circles, green triangles, purple X's, and the cyan square represent functionals of LDA, GGA, mGGA, hGGA, and dhGGA type, respectively.

only in their parametrization of the uniform electron gas, and do a poor job of predicting densities and atomization energies relative to other functional types. Functionals of GGA type (red circles) show no correlation between density error and atomization energy error, exhibiting a narrow range of values for the density error and a wide variation of atomization energy errors. Functionals of meta-GGA type (green triangles) show a positive correlation between density errors and atomization energy errors. Functionals of hGGA type (purple X's) lack a clear correlation between the density error and atomization energy error and show variation of both types of errors within the functionals studied.

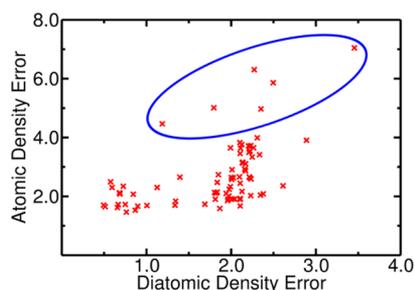
Thus, the hGGA functionals were further investigated by plotting the same data as in Figure 3 but separating the hGGA functionals into functionals developed before and after the year 2000, as given in Figure 4. The year 2000 is chosen as the



**Figure 4.** Plot of density error, as given in eq 3, versus mean absolute atomization energy error, as given in eq 4, for the 36 hGGA functionals in this study. Blue and red '+'s represent hGGA functionals developed before and after the year 2000, respectively.

dividing point because the previous study observed an upward trend in density error for functionals beginning in 2000. The difference between the early and late development of hGGA functionals is immediate: hGGA functionals developed before the year 2000 exhibit a high degree of correlation between the density error and atomization energy error, while hGGA functionals developed after the year 2000 do not exhibit any correlation. All of the hGGA functionals developed after the year 2000 predict relatively accurate atomization energies but show significant variation in the electron densities, supporting the hypothesis that recent functional development has focused on improving energy and other properties at the expense of the density. However, previous work<sup>27</sup> has suggested that an accurate density may not significantly influence the computed atomization energies of these diatomics because the errors in energy for atoms and closed shell molecules near equilibrium are typically dominated by errors due to the use of an approximate functional rather than the use of an approximate density.

For functionals used in both the present study and the previous study on atoms, the relative ability of the functionals to compute densities for diatomics versus atoms is compared in Figure 5. In this figure, the two measures of density error are



**Figure 5.** Plot of density error for diatomics (present study) versus atomic density error (previous study<sup>20</sup>) for the 82 functionals common to both studies. The red X's circled in blue are outlying functionals that perform better for computing diatomic densities than atomic densities. An additional plot with a measure of atomic density error that depends only on the error of the electron density rather than the electron density, gradient, and Laplacian is presented in Figure S1 of the Supporting Information.

different, so the relative absolute values of the diatomic and atomic density errors are not meaningful. Most functionals show a similar degree of correlation between the diatomic and atomic density error, but six functionals deviate from this trend. These functionals are the M06-HF,<sup>28</sup> M11,<sup>29</sup> M11-L,<sup>30</sup> SOGGA11,<sup>31</sup> N12,<sup>32</sup> and N12-SX<sup>33</sup> functionals of the Minnesota functional family and are circled in blue in Figure 5. These Minnesota functionals are the six weakest performing functionals for predicting atomic densities, but they perform significantly better than expected for the computation of diatomic densities, on the basis of the performance of all other functionals studied. This analysis suggests that using atomic densities as the sole metric for judging the ability of functionals to accurately predict densities may not be sufficient for chemical systems.

The results of the present study agree predominantly with the calculations on atoms of the recent study.<sup>20</sup> In particular, beginning in the early 2000s, improvements in DFT functionals for energies do not always correspond to an equivalent improvement in the calculated electron density, even in the chemical bonding region. In spite of the present and recent results demonstrating errors in the densities for some functionals, a philosophical question remains as to the purpose of DFT functional development. Is the purpose to approximate the exact functional or simply to provide chemists with a useful tool for exploring chemical systems? Functionals developed through the use of empirically fitted parameters have been successfully applied to many chemical systems. Therefore, the observation that many modern functionals produce incorrect densities could be of no great consequence for many studies that simply employ DFT as a computational tool for calculating geometries and energies. However, these functionals are unlikely to perform well for predicting properties that depend on the density, such as dipole moments or charge distribution analyses. Moreover, from a rigorous theoretical perspective, they are straying from the path toward the exact functional. Although the debate over the optimal strategy for current functional development is not likely to end soon, the ultimate goal is still to obtain both accurate densities and accurate energies.

## COMPUTATIONAL METHODS

Calculations with the APFD,<sup>34</sup> HISSBPBE,<sup>35</sup> MN12-L,<sup>36</sup> MN12-SX,<sup>33</sup> N12,<sup>32</sup> and N12-SX<sup>33</sup> functionals were performed using Gaussian09,<sup>37</sup> and all other calculations were performed using GAMESS.<sup>38</sup> The integration grid was chosen by specifying GRID = JANS2 in GAMESS and GRID = SuperFineGrid in Gaussian. The JANS2 grid consists of 155 radial points for all atoms and an angular Lebedev grid with a largest size of 974 points. The SuperFineGrid is a pruned grid with 175 974 points for first-row atoms and 250 974 points for nonfirst-row atoms. Calculations on Li<sub>2</sub> with the M11-L<sup>30</sup> and M11<sup>29</sup> functionals, Na<sub>2</sub> with the M06-HF<sup>28</sup> and M11-L functionals, and Si<sub>2</sub> with the M11-L functional failed to converge with the aug-cc-pCVQZ basis set, so for these systems, the aug-cc-pVQZ<sup>39</sup> basis set was used to compute the density. Reference CCSD calculations were performed on each diatomic and constituent atom with the aug-cc-pCVQZ basis set. For the CCSD calculations, no frozen core was used. The diatomic molecule calculations that failed to converge using the aug-cc-pCVQZ basis set and instead were performed using the aug-cc-pVQZ basis set were excluded from the calculation of

the MAAEE to ensure a consistent basis set for the energy calculations.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.jpcllett.7b00774](https://doi.org/10.1021/acs.jpcllett.7b00774).

Density errors and MAAEEs for all functionals; bond lengths of the diatomics; and a variant of Figure 5 plotted with the atomic density error constructed solely from the error of the density (PDF)

Atomization energies, on-axis density errors, and off-axis density errors for all functionals and molecules (XLSX)

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### Notes

The authors declare no competing financial interest.

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