

## Insensitivity of the error of the minimally empirical hybrid functional revTPSSh to its parameters

Robin Haunschild, John P. Perdew, and Gustavo E. Scuseria

Citation: *J. Chem. Phys.* **137**, 224104 (2012); doi: 10.1063/1.4769790

View online: <http://dx.doi.org/10.1063/1.4769790>

View Table of Contents: <http://jcp.aip.org/resource/1/JCPSA6/v137/i22>

Published by the [American Institute of Physics](#).

---

### Additional information on *J. Chem. Phys.*

Journal Homepage: <http://jcp.aip.org/>

Journal Information: [http://jcp.aip.org/about/about\\_the\\_journal](http://jcp.aip.org/about/about_the_journal)

Top downloads: [http://jcp.aip.org/features/most\\_downloaded](http://jcp.aip.org/features/most_downloaded)

Information for Authors: <http://jcp.aip.org/authors>

## ADVERTISEMENT



**Goodfellow**  
metals • ceramics • polymers • composites  
70,000 products  
450 different materials  
**small quantities fast**

[www.goodfellowusa.com](http://www.goodfellowusa.com)

# Insensitivity of the error of the minimally empirical hybrid functional revTPSSh to its parameters

Robin Haunschild,<sup>1,a)</sup> John P. Perdew,<sup>1,2</sup> and Gustavo E. Scuseria<sup>1,3,4</sup>

<sup>1</sup>Department of Chemistry, Rice University, Houston, Texas 77005, USA

<sup>2</sup>Department of Physics and Engineering Physics, Tulane University, New Orleans, Louisiana 70118, USA

<sup>3</sup>Department of Physics and Astronomy, Rice University, Houston, Texas 77005, USA

<sup>4</sup>Chemistry Department, Faculty of Science, King Abdulaziz University, Jeddah 21589, Saudi Arabia

(Received 9 September 2012; accepted 19 November 2012; published online 11 December 2012)

We investigate the parameter dependence of the error of the hybrid of the revised Tao-Perdew-Staroverov-Scuseria (revTPSSh) density functional for the exchange-correlation energy within popular molecular test sets. In particular, we allow for satisfaction of a possibly tighter Lieb-Oxford lower bound on the exchange-correlation energy. We are able to improve over the original revTPSSh on average, but in total the variation of the performance of revTPSSh seems to be low when its parameters are changed. We recommend to continue using the original revTPSSh variant rather than our fitted versions, because we expect a broader applicability from the original parameter set.

© 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4769790>]

## I. INTRODUCTION

Kohn-Sham (KS) density functional theory (DFT) has emerged as a very important method to study ground-state energies and electron densities.<sup>1</sup> The lowest three rungs of the density functional approximation (DFA) ladder [local (LDA), gradient corrected (GGA), and meta-GGA (MGGA) functionals] can be constructed without empirical parameters, by satisfaction of exact constraints, while still obtaining a good performance compared to other DFAs within the same rung.<sup>2,3</sup> Using hyper-GGAs (also called hybrids) located on the fourth rung, some empiricism seems to be unavoidable when a good performance is expected.<sup>4</sup>

The dependence of the functional's performance on its parameters is an important indicator for its universal applicability. This holds true for the empirical as well as the non-empirical parameters. One of the best performing non-empirical meta-GGA functionals is revTPSS (revised Tao-Perdew-Staroverov-Scuseria).<sup>5</sup> The performance of revTPSS is good not only for molecules<sup>5</sup> but even for the lattice constants<sup>5-7</sup> and surface energies<sup>5,6</sup> of solids, and for the binding of a CO molecule to a transition-metal surface.<sup>6</sup> Analogously to its predecessor,<sup>8</sup> a global hybrid can be constructed by admixing 10% of exact exchange with 90% of revTPSS exchange giving rise to revTPSSh.<sup>9</sup>

The aim of this work is to study the dependence of the revTPSSh error on its parameters. revTPSSh contains five parameters aside from those fitted to gradient expansions and other strong constraints. Four ( $\kappa$ ,  $\mu$ ,  $c$ , and  $e$ ) of them are considered to be non-empirical, while the portion of admixed exact exchange ( $a_0$ ) is considered to be empirical. Three of them ( $\kappa$ ,  $\mu$ , and  $a_0$ ) can be fitted to suitable test sets, while still satisfying the same exact constraints as the original revTPSSh. The parameters  $c$  and  $e$  can be chosen to sat-

isfy the same constraints (hydrogen atom energy and derivative constraint of the enhancement factor) as in revTPSS. Alternatively, they could also be relaxed to provide better performance within training sets. We explore these possibilities in this study. Goerigk and Grimme<sup>10</sup> have varied parameters in the original TPSS meta-GGA,<sup>8</sup> which is less accurate for solids than revTPSS. They found little overall improvement of main-group chemical properties in their GMTKN24 data set,<sup>10</sup> without inclusion of long-range dispersion corrections. We thought that turning to the hybrid revTPSSh and varying its fraction of exact exchange along with the other parameters might change the story, but in fact it did not. Section II gives details on our calculations. Our results are discussed in Sec. III. Finally, we present our conclusions in Sec. IV.

## II. COMPUTATIONAL DETAILS

The development version of the GAUSSIAN electronic structure program<sup>11</sup> has been used for the calculations in this study. All calculations employ the fully uncontracted 6-311++G(3df, 3pd) basis set<sup>12,13</sup> to obtain benchmark quality results. For numerical integration of the DFT XC potential, we use the UltraFine grid with 99 radial shells and 590 angular points.

The rather large training sets G2/97 (148 molecules)<sup>14</sup> and BH42/03 (21 forward and reverse hydrogen transfer barrier heights)<sup>15</sup> are used to fit empirical parameters. The superset of G2/97 and G3-3 (75 molecules)<sup>16</sup> (a total of 223 molecules comprising the G3/99 test set)<sup>17,18</sup> as well as the barrier height test sets HTBH38/04 (19 forward and reverse hydrogen transfer barrier heights)<sup>15</sup> and NHTBH38/04 (19 forward and reverse non-hydrogen transfer barrier heights)<sup>19</sup> are employed for assessment of the fitted functionals. The employed geometries and reference values are available from the supporting information of Ref. 20. They are on the B3LYP/6-31G(2df, p) level of theory for the G3/99 test set and on the

<sup>a)</sup> Author to whom correspondence should be addressed. Electronic mail: H@unschuld.de.

QCISD/MG3 level of theory for the HTBH38/04, BH42/03, and NHTBH38/04 test sets. Calculations of heats of formation used zero-point energies on the B3LYP/6-31G(2df, p) level of theory with a frequency scale factor of 0.9854 as recommended in Ref. 21. There are theoretical atomization energies available for the G2/97 test set,<sup>22</sup> but for the purpose of our study the experimental heats of formation are at least as suitable.

Calculations of open-shell species were carried out via spin-unrestricted formalisms. Errors are reported as *calculated-reference*.

### III. RESULTS

revTPSSh has several parameters fixed by density gradient expansions and other strong constraints, and those we will not adjust. Its other parameters are

$$a_0 = 0.10, \kappa = 0.804, \mu = 0.14, c = 2.35204, \text{ and} \\ e = 2.1677 \text{ (revTPSSh)}.$$

The fraction  $a_0$  of exact exchange is an empirical parameter fitted to atomization energies of molecules. The parameter  $\kappa$  controls the large-gradient limit of the exchange energy, and is set to the largest value required to satisfy the Lieb-Oxford lower bound on the exchange energy (as in the PBE<sup>23</sup> and PBEsol<sup>24</sup> GGA's). The parameter  $\mu$  controls the approach of the exchange energy to its large-gradient limit, and is set to a PBEsol-like value. The parameters  $c$  and  $e$  are adjusted to achieve simultaneously the exact exchange-correlation energy for the hydrogen atom and other one-electron atomic ions and to zero out the spurious singularity in the meta-GGA exchange potential at the nucleus.

In order to conserve the Lieb-Oxford<sup>25</sup> bound for all possible electron densities, any fitted revTPSSh version has to obey the constraint  $\kappa \leq 0.804$ . There have been recent suggestions (e.g., Ref. 4) that  $\kappa$  should be less than 0.804. The parameter  $\mu$  has to be non-zero and positive so that no known exact constraints are violated. The parameters  $c$  and  $e$  were set to satisfy the hydrogen atom energy and the derivative constraint,  $\left. \frac{dF_x(s, \alpha=0)}{ds} \right|_{s=0.376} = 0$ , not for the exact density as in Refs. 5 and 8 but for the self-consistent density within our finite basis set. Starting at the original parameter set we minimized the absolute deviation from the hydrogen atom energy and the derivative constraint where we allowed  $c$  and  $e$  to vary. Parameter  $e$  mainly influences the value of the derivative of the enhancement factor and less so the hydrogen atom energy, while parameter  $c$  has a significant influence on both values. As we fit for a different density than the original revTPSS was constructed for, the value of  $c$  differs from the original value. Calculation of the derivative of the enhancement factor is not altered by the employed density. Thus, parameter  $e$  does not change compared to its original value. The resulting variants are referred to as revTPSSI and revTPSShI. They have the same values for  $\kappa$ ,  $\mu$ , and  $e$  as their parent functionals, but a slightly different value for  $c$  of 2.34385. The performance within the considered test sets is essentially the same for revTPSS and revTPSSI as well as for revTPSSh and revTPSShI (revTPSShI has a mean absolute error, MAE, for

BH42/03 higher by 0.1 kcal/mol, and revTPSSI has a slightly higher MAE for G3-3 and G3/99 by 0.2 and 0.1 kcal/mol, respectively, while the other statistical values are the same).

We tested different fitting strategies starting in different parts of the parameter space. We show the versions which differ most compared to the original revTPSSh. We found the following local minima in parameter space:

- (1)  $a_0 = 0.13, \kappa = 0.70, \mu = 0.14, c = 2.782$ , and  $e = 2.542$  referred to as revTPSSh3a,
- (2)  $a_0 = 0.19, \kappa = 0.68, \mu = 0.14, c = 2.781$ , and  $e = 2.542$  referred to as revTPSSh3b, and
- (3)  $a_0 = 0.14, \kappa = 0.77, \mu = 0.07, c = 2.49$ , and  $e = 0.77$  referred to as revTPSSh3c.

The variant revTPSSh3a was fitted to minimize the subset-weighted error:

$$SW = \text{MAE(G2/97)} + 1000(|\text{deriv. error}| + |\text{H atom error}|), \quad (1)$$

while revTPSSh3b was fitted to

$$SW = 0.5 [\text{MAE(G2/97)} + \text{MAE(BH42/03)}] \\ + 1000(|\text{deriv. error}| + |\text{H atom error}|), \quad (2)$$

and revTPSSh3c was fitted to

$$SW = 0.5 [\text{MAE(G2/97)} + \text{MAE(BH42/03)}]. \quad (3)$$

Thus, revTPSSh3a and revTPSSh3b fulfill the same exact constraints as revTPSSh while revTPSSh3c does not. The latter violates the derivative constraint by 0.132 a.u. and the hydrogen atom energy by 0.00354 a.u. The high weights of the exact constraints in the fitting function  $SW$  for revTPSSh3a and revTPSSh3b were chosen to ensure very tight satisfaction of these constraints. Interestingly, the parameter  $\mu$  has the same value for revTPSSh3a and revTPSSh3b as well as for the original revTPSSh, while revTPSSh3c has a significant smaller value of the parameter  $\mu$ . This indicates that the parameter  $\mu$  is rather important to satisfy the derivative and hydrogen atom energy constraints. Parameter  $c$  is raised in all our fitted versions compared to the original value. The variants revTPSSh3a and revTPSSh3b use a higher value for the parameter  $e$  than revTPSSh while a much lower value is used for revTPSSh3c. The parameter sets of the versions revTPSSh3a and revTPSSh3b mainly differ from each other in the exact exchange admixture. This indicates that a lower  $\kappa$  value requires a larger value of the parameters  $c$  and  $e$  in order to fulfill the exact constraints imposed on both revTPSSh3a and revTPSSh3c as well as the original revTPSSh. The parameter set we obtained for revTPSSh3c shows that disregarding the derivative and hydrogen atom energy constraints provides the possibility to improve the average error within a certain training set.

Table I presents the mean errors (ME) and mean absolute errors (MAE) for revTPSS, revTPSSh, and our fitted versions revTPSSh3a-revTPSSh3c for heats of formation and barrier heights. The upper part of Table I contains the test sets used for fitting, while the middle part shows the performance for other test sets. Note that HTBH38/04 is a subset of BH42/03 and G3/99 is the superset of G2/97 and G3-3.

TABLE I. ME (mean error) and MAE (mean absolute error) values in kcal/mol in common molecular test sets and derivative error and hydrogen atom energy error in atomic units using the uncontracted 6-311++G(3df, 3pd) basis set for revTPSS, revTPSSh, and revTPSSh3a - revTPSSh3c.

Test set	revTPSS		revTPSSh		revTPSSh3a		revTPSSh3b		revTPSSh3c	
	ME	MAE	ME	MAE	ME	MAE	ME	MAE	ME	MAE
G2/97	-4.7	5.7	-1.2	4.5	-1.7	5.0	-0.4	5.8	0.3	3.7
BH42/03	-7.6	7.6	-6.0	6.0	-5.9	5.9	-5.1	5.1	-5.2	5.2
G3-3	-4.2	4.7	0.6	3.6	-2.5	4.8	-1.3	5.7	3.5	4.4
G3/99	-4.5	5.4	-0.6	4.2	-1.8	5.0	-0.7	5.7	1.4	3.9
HTBH38/04	-7.4	7.4	-5.8	5.8	-5.6	5.6	-4.8	4.8	-4.9	4.9
NHTBH38/04	-9.3	9.3	-7.1	7.2	-6.8	6.8	-5.6	5.7	-6.9	6.9
Deriv. error		0.00046			-0.00008		-0.00001		0.13176	
H atom error	0.00002		0.00005		-0.00003		-0.00026		-0.00354	

Additionally, the lower part of Table I presents deviations from the derivative and hydrogen atom energy constraints. The average performance of revTPSSh3a within the fitting test sets is worse than the original revTPSSh which is in part due to the high weight of the exact constraints in the fitting function  $SW$ . The exact constraints are fulfilled very well by revTPSSh3a and revTPSSh3b. Both exact constraints are significantly violated by revTPSSh3c where we did not include the exact constraints in the fitting procedure. This leads to a better performance of revTPSSh3c within the fitting test sets G2/97 and BH42 compared to all other functionals in Table I. Our revTPSSh3c also outperforms revTPSSh3a and revTPSSh3b for the G3-3 test set which was not considered in the fitting procedure. The original revTPSSh, however, performs even better for the G3-3 test set than revTPSSh3c. For the non-hydrogen transfer barrier heights (NHTBH38/04), revTPSSh3c performs slightly better than the original revTPSSh but worse than revTPSSh3a and revTPSSh3b. Overall we do not see much benefit of fitting the parameters in revTPSSh to test sets with or without satisfaction of exact constraints. This suggests that the performance of revTPSSh does not change much upon a change of the numerical values of its parameters.

Besides minima referred to as revTPSSh3i we also found other minima closer to the original parameter set of revTPSSh. The lowest minimum we found has the parameter set:

$$a_0 = 0.15, \kappa = 0.797, \mu = 0.14, c = 2.3437, \text{ and } e = 2.16778.$$

It was obtained according to the fitting strategy of revTPSSh3b but with a different starting point in the parameter space. This means that this variant also obeys the same exact constraints as revTPSSh. The main difference is in the exact exchange admixture while the other parameters are very close to the original values of revTPSSh. It improves over revTPSSh for barrier heights but worsens the description of heats of formation. As our focus in this study is to find variants of revTPSSh with different values for  $\kappa$ ,  $\mu$ ,  $c$ , and  $e$ , we neglect this variant from now on.

In order to test how much the performance of the functionals revTPSSh3a-revTPSSh3c changes for the test set

G3/99 between the optimized and original values, we step the parameter  $a_0$  from its revTPSShI value (0.10) to its variant value in  $N$  equal steps of 0.01, allowing each of the other parameters ( $\kappa$ ,  $\mu$ ,  $c$ , and  $e$ ) to change in  $N$  equal steps from its revTPSShI to its variant value. In other words, we move in equal steps along a parameter vector from revTPSShI to any of its variants. The results are shown in Figure 1. The variants revTPSSh3a and revTPSSh3b show a very similar monotonous increase of MAE for the G3/99 test set upon a linear change in parameter values. On our path through the parameter space from revTPSShI to revTPSSh3c we encounter a maximum of MAE for G3/99 around  $a_0 = 0.12$ . Although we see variation in MAE of the G3/99 test set when the parameters  $a_0$ ,  $\kappa$ ,  $\mu$ ,  $c$ , and  $e$  of revTPSSh are changed, there is no significant change of overall performance, as the MAE values stay within a range of  $\pm 1$  kcal/mol if all exact constraints of revTPSSh are kept. Overall, Figure 1 supports our previous conclusion that the performance of revTPSSh does not change too much when its parameters are changed, especially if the same exact constraints are obeyed as for revTPSSh. This also indicates that the original parameter set is already quite close to an optimal parameter set for this type of functional,

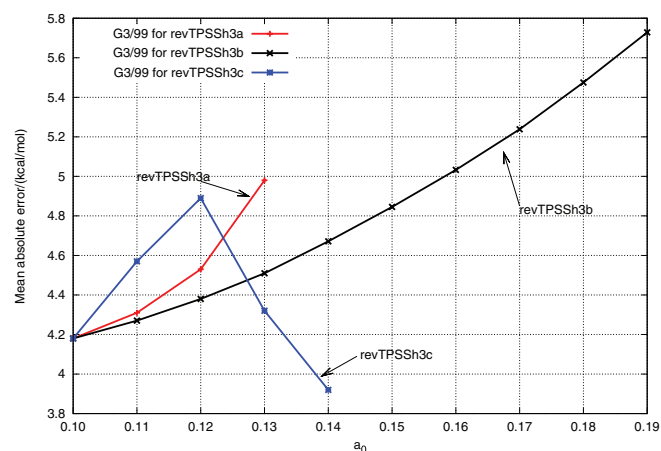


FIG. 1. Performance of revTPSSh3a (red), revTPSSh3b (black), and revTPSSh3c (blue) for the G3/99 test set, moving along a straight line in parameter space between their parameter values and ones of revTPSShI at  $a_0 = 0.10$ . Note that satisfaction of the derivative and H-atom constraints is expected to be better at each end of each curve than it is in between.



although it was not fitted to test sets. As Figure 1 suggests a better performance for  $a_0 > 0.14$  in the case of revTPSSh3c we also calculated a step further along the parameter vector to  $a_0 = 0.15$ . This leads to a high increase in MAE for heats of formation (MAE of 8.8 kcal/mol for G2/97) and a modest decrease in MAE for barrier heights (MAE of 4.3 kcal/mol for BH42). We attribute this rather large increase of MAE for heats of formation to unphysical parameter set values, especially in the case of  $e$  and  $\mu$  ( $e = 0.42058$  and  $\mu = 0.05250$ ) for  $a_0 = 0.15$ . Having this in mind, we calculated another point before revTPSSh3c is reached at  $a_0 = 0.135$ . The MAE of G3/99 drops to 3.7 kcal/mol which is due to the G3-3 test set where the MAE drops to 3.2 kcal/mol (from 4.2 kcal/mol) when  $a_0$  is changed from 0.13 to 0.135. The MAE of G2/97 deviates only slightly from a linear interpolation between its MAE values at  $a_0 = 0.13$  and  $a_0 = 0.14$ . This highlights the significance of exact constraints. This strange behavior of revTPSSh3c is probably due to neglecting two important exact constraints, the derivative value of the enhancement factor and the hydrogen atom energy. We expect our observations made for the variants revTPSSh3a and revTPSSh3b to also hold true for the other test sets of similar properties.

#### IV. CONCLUSIONS

We singled out adjustable parameters in the functional revTPSSh which were adjusted to fitting test sets. The fitting procedure was carried out with and without satisfying exact constraints. Overall, the best performance is reached when the exact constraints are not imposed, but the performance is only slightly better than for the other variants and for the original revTPSSh. This indicates that the performance of revTPSSh does not change much when the values of its parameters are changed. This also suggests that the original parameter set—although not fitted—is quite close to being optimal. In particular, the performance of the revTPSSh form is not improved much by any hypothetical tightening of the Lieb-Oxford lower bound on the exchange-correlation energy. We found a variant which mainly differs from revTPSSh in the amount of exact exchange admixed. This version improves over revTPSSh for barrier heights, but performs worse than revTPSSh for heats of formation. Due to the small overall benefit of relaxing the parameters of revTPSSh, we recommend to continue using the original revTPSSh. We expect a broader applicability from the original parameter set than from our fitted ones.

#### ACKNOWLEDGMENTS

The work at Rice University was supported by the National Science Foundation (NSF) under CHE-1110884 and the Welch Foundation (C-0036). R.H. thanks the Deutsche Forschungsgemeinschaft (DFG, Grant No. HA 5711/2-1). J.P.P. acknowledges the support of the National Science Foundation through Grant No. DMR-0854769 and Cooperative Agreement No. EPS-1003897 with support from the Louisiana Board of Regents. The authors thank Carlos A. Jiménez-Hoyos and Dr. Thomas M. Henderson for their original implementation of the revTPSSh functional.

- <sup>1</sup>W. Koch and M. C. Holthausen, *A Chemist's Guide to Density Functional Theory* (Wiley VCH, Weinheim, 2001).
- <sup>2</sup>J. P. Perdew and K. Schmidt, *AIP Conf. Proc.* **577**, 1 (2001).
- <sup>3</sup>J. P. Perdew, A. Ruzsinszky, J. Tao, V. N. Staroverov, G. E. Scuseria, and G. I. Csonka, *J. Chem. Phys.* **123**, 062201 (2005).
- <sup>4</sup>R. Haunschild, M. M. Odashima, G. E. Scuseria, J. P. Perdew, and K. Capelle, *J. Chem. Phys.* **136**, 184102 (2012).
- <sup>5</sup>J. P. Perdew, A. Ruzsinszky, G. I. Csonka, L. A. Constantin, and J. Sun, *Phys. Rev. Lett.* **103**, 026403 (2009).
- <sup>6</sup>J. Sun, M. Marsman, A. Ruzsinszky, G. Kresse, and J. P. Perdew, *Phys. Rev. B* **83**, 121410 (2011).
- <sup>7</sup>P. Hao, Y. Fang, J. Sun, G. Csonka, P. H. T. Philipsen, and J. P. Perdew, *Phys. Rev. B* **85**, 014111 (2012).
- <sup>8</sup>J. Tao, J. P. Perdew, V. N. Staroverov, and G. E. Scuseria, *Phys. Rev. Lett.* **91**, 146401 (2003).
- <sup>9</sup>G. I. Csonka, J. P. Perdew, and A. Ruzsinszky, *J. Chem. Theory Comput.* **6**, 3688 (2010).
- <sup>10</sup>L. Goerigk and S. Grimme, *J. Chem. Theory Comput.* **6**, 107 (2010).
- <sup>11</sup>M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, GAUSSIAN development version, Revision H.01, Gaussian, Inc., Wallingford, CT, 2009.
- <sup>12</sup>A. D. McLean and G. S. Chandler, *J. Chem. Phys.* **72**, 5639 (1980).
- <sup>13</sup>R. Krishnan, J. S. Binkley, R. Seeger, and J. A. Pople, *J. Chem. Phys.* **72**, 650 (1980).
- <sup>14</sup>L. A. Curtiss, K. Raghavachari, P. C. Redfern, and J. A. Pople, *J. Chem. Phys.* **106**, 1063 (1997).
- <sup>15</sup>Y. Zhao, B. J. Lynch, and D. G. Truhlar, *J. Phys. Chem. A* **108**, 2715 (2004).
- <sup>16</sup>L. A. Curtiss, K. Raghavachari, P. C. Redfern, and J. A. Pople, *J. Chem. Phys.* **112**, 7374 (2000).
- <sup>17</sup>V. N. Staroverov, G. E. Scuseria, J. Tao, and J. P. Perdew, *J. Chem. Phys.* **119**, 12129 (2003); **121**, 11508 (2004).
- <sup>18</sup>COF<sub>2</sub> was included in the G2/97 and G3/99 test sets following Ref. 17.
- <sup>19</sup>Y. Zhao, N. González-García, and D. G. Truhlar, *J. Phys. Chem. A* **109**, 2012 (2005); **109**, 4942 (2006).
- <sup>20</sup>R. Haunschild, B. G. Janesko, and G. E. Scuseria, *J. Chem. Phys.* **131**, 154112 (2009).
- <sup>21</sup>L. A. Curtiss, P. C. Redfern, K. Raghavachari, and J. A. Pople, *J. Chem. Phys.* **114**, 108 (2001).
- <sup>22</sup>R. Haunschild and W. Klopper, *J. Chem. Phys.* **136**, 164102 (2012).
- <sup>23</sup>J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- <sup>24</sup>J. P. Perdew, A. Ruzsinszky, G. I. Csonka, O. A. Vydrov, G. E. Scuseria, L. A. Constantin, X. Zhou, and K. Burke, *Phys. Rev. Lett.* **100**, 136406 (2008).
- <sup>25</sup>E. H. Lieb and S. Oxford, *Int. J. Quantum Chem.* **19**, 427 (1981).