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A new family of hybrid density functionals

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Abstract

A new family of (range-separated) hybrid functionals is presented that corrects several of the shortcomings of the recently reported SSB-D functional. The new functionals include Grimme's D_3 dispersion energy, contain a reduced number of parameters which have been optimized against a number of different interaction types. When comparing the new functionals with over thirty other density functionals, the new hybrid functional S12h and its range-separated analogue CAM-S12h are found to be the best performing ones for the different interaction types. The performance for spin states is poor for the hybrid functionals, but very well for the GGA counterpart S12g.

Keywords

Density Functional Theory – Reaction barriers – Spin states – Weak interactions.

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I. INTRODUCTION

Density functional theory[1] has become arguably the most widely used computational tool for chemical research on medium-sized and larger molecules (20-200 atoms). In part this is due to its efficiency, but also because of the major improvements for describing weakly-bound systems through the use of dispersion energy contributions.[2] Apart from some recent advances based on the density itself,[3,4] probably the most widely used approach for dealing with the dispersion energy is obtained with Grimme's empirical schemes[2] (DFT-D_2 and DFT-D_3). The Grimme approach however needs parameters that are specific for each functional, and some authors argue even for using basis-set dependent parameters.[5] Moreover, these parameters are usually obtained[2] after the design of the density functional itself, and therefore the combination of a given functional with its empirical dispersion contribution may not be optimal. Because of that, a few years ago we reported a few years ago the SSB-D functional[6] in which the parameters for the DFT-D_2 dispersion energy were included from the start in the design of the functional. As a result, the SSB-D functional performed well for intra- and intermolecular dispersion interactions[7] (*water hexamers, noble-gas dimers,* $C_{12}H_{12}$ *isomers, branching of octane, dissociation of anthracene, stacked adenine dimers*), although this has been righteously criticized by Goerigk and Grimme[8] who looked at other weakly-bound systems. Another point of criticism[8] was the larger total electronic energies with SSB-D, which gives for water a value of around -77.005 Hartree with e.g. Jensen's polarization-consistent pcS-4 basis set,[9] while at CCSD(T)/pcS-4 this value is -76.427 Hartree (close to the experimental estimated[8] value of -76.432 Hartree). This difference comes almost entirely from the exchange part of SSB-D, which for atoms indeed overestimates the exchange energy (vide infra). Here, new density functionals are described that do not suffer from this drawback. Moreover, they include Grimme's newer

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(D_3) dispersion contribution that was shown to be performing much better[2] than the previous D_2 one.

II. FORMULATION OF THE DENSITY FUNCTIONALS

The energy in standard pure density functional theory is obtained as a modification of the local density approximation (LDA) where the only ingredient is the electron density ρ.[1] There are several more sophisticated approximations that take more density ingredients into account, such as the density gradient ($\nabla\rho$) in generalized gradient approximations (GGA), and the Laplacian of the density ($\nabla^2\rho$) and/or the kinetic energy density τ in mGGA functionals (see eq. 1).[1]

$$\begin{aligned}
E_{XC}^{LDA}\left[\rho_\alpha,\rho_\beta\right] &= \int d^3r\ \ \varepsilon_{XC}^{unif}\left(\rho_\alpha,\rho_\beta\right)\\
E_{XC}^{GGA}\left[\rho_\alpha,\rho_\beta\right] &= \int d^3r\ \ f\left(\rho_\alpha,\rho_\beta,\nabla\rho_\alpha,\nabla\rho_\beta\right)\\
E_{XC}^{mGGA}\left[\rho_\alpha,\rho_\beta\right] &= \int d^3r\ \ f\left(\rho_\alpha,\rho_\beta,\nabla\rho_\alpha,\nabla\rho_\beta,\nabla^2\rho_\alpha,\nabla^2\rho_\beta,\tau_\alpha,\tau_\beta\right)
\end{aligned} \tag{1}$$

This energy can be improved upon by taking a portion of Hartree-Fock exchange in hybrid functionals,[10] and by including a dispersion contribution such as the one by Grimme[2] (eq. 2).

$$E_{tot} = a_x \cdot E_{x,HF} + b_x \cdot E_{x,LDA/(m)GGA} + E_{c,LDA/(m)GGA} + E_{disp} \tag{2}$$

In this latter equation, $E_{x,HF}$ stands for the Hartree-Fock exchange energy, $E_{x,LDA/(m)GGA}$ for the exchange part of E_{xc}, $E_{c,LDA/(m)GGA}$ for the correlation part of E_{xc}, and E_{disp} for the dispersion energy. The parameters a_x and b_x can be chosen independently ($a_x+b_x\neq1$) or constrained to fulfill $a_x+b_x=1$ (which is done here). In recent years, range-separated (also known as long-range corrected, LC) functionals[11-17] have become more popular, in which the long-range potential of density functionals is improved with an Ewald split of r_{12}^{-1} using the error function (eq. 3):

$$\frac{1}{r_{12}} = \frac{1-\operatorname{erf}\left(\mu \cdot r_{12}\right)}{r_{12}} + \frac{\operatorname{erf}\left(\mu \cdot r_{12}\right)}{r_{12}} \tag{3}$$

The first term accounts for the short-range interactions and is described by the LDA/(m)GGA functional, while the second term accounts for the long-range interactions with Hartree-Fock exchange. Here the terminology of the Coulomb-attenuated method (CAM)[13] by Handy and co-workers is used, who generalized eq. 3 into the following form:

$$\frac{1}{r_{12}} = \frac{1-\left[\alpha + \beta \cdot \operatorname{erf}\left(\mu \cdot r_{12}\right)\right]}{r_{12}} + \frac{\alpha + \beta \cdot \operatorname{erf}\left(\mu \cdot r_{12}\right)}{r_{12}} \tag{4}$$

In eq. 4 there are now three CAM-parameters (α, β and μ), for which the relations $0 \leq \alpha+\beta \leq 1$, $0 \leq \alpha \leq 1$ and $0 \leq \beta \leq 1$ should hold; for their CAM-B3LYP functional Handy and co-workers used[13] values of 0.19 (α), 0.46 (β) and 0.33 (μ).

In the current contribution four new functionals are reported: (i) a GGA functional (S12g), (ii) a hybrid equivalent of it (S12h), (iii) a CAM-version of the GGA functional (CAM-S12g) and (iv) a CAM-version of the hybrid functional (CAM-S12h). The formulation of the GGA part in all these functionals is loosely based on the ones used in PBE[18] and SSB-D,[6] but rewritten in a different way. Similar to the procedure in SSB-D, a standard correlation functional is taken which is in this case chosen as the PBEc one (together with its PW92 LDA part):

$$E_{s12g} = E_{s12g,X} + E_{PBE,c} + E_{disp,D3} \tag{5}$$

For the exchange part and the enhancement factor $F_{s12g}(x)$, let's start with the (s)PBE expressions[6,18] for the exchange enhancement factor and the gradient contribution H to the correlation part (rewritten slightly compared to the original papers):

$$\begin{aligned} F_{PBE,X}(s) &= 1 + K_{PBE}\left[1 - \frac{1}{1 + L_{PBE}s^2}\right] \quad ; \quad L_{PBE} = \mu_{PBE}/K_{PBE} \\ H_{PBE,C}(t) &= W_{PBEc} \cdot \ln\left(1 + U_c \cdot \left[1 - \frac{1}{1 + Gt^2 + G^2t^4}\right]\right) \\ H_{sPBE,C}(t) &= W_{PBEc} \cdot \ln\left(1 + U_c \cdot \left[1 - \frac{1}{1 + Gt^2}\right]\right) \end{aligned} \tag{6}$$

In these expressions, some factors are grouped together (in W_{PBEc} and U_c) to make the comparison between both parts more clearly visible, while G in these equations is in fact a function of the LDA correlation energy (it is called A in the PBE paper[18]). The important thing to notice here is the part in square brackets that contains in the denominator only a second order term (s^2) for exchange but both a second-order and a fourth-order term (t^2, t^4) for correlation; both s and t are dimensionless density gradients as defined[18] by Perdew and co-workers. In SSB-D,[6] the PBE enhancement factor for exchange was used together with a simplification of the correlation part (*sPBE* expression[6] in eq. 6) to have only second-order terms in both exchange and correlation; here it is done the other way around, by adapting the exchange term to include fourth order terms as well. Moreover, in order to achieve a flat profile for low values of s (or rather, in terms of its analogous variable $x=|\nabla\rho|/\rho^{4/3}$;

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$s=x/[2\cdot(3\pi^2)^{1/3}]$), here a slightly different form is taken (with *A*, *B*, *C*, *D* and *E* parameters to be determined later):

$$\begin{aligned} F_{s12g,X}\left(x_i\right) &= A + B\cdot\left[1-\frac{1}{1+Cx_i^2+Dx_i^4}\right]\cdot\left[1-\frac{1}{1+Ex_i^2}\right] \\ E_{s12g,X} &= \sum_{i=\alpha,\beta} C_{LDA,X}\cdot\rho_i^{4/3}\cdot F_{s12g}\left(x_i\right) \end{aligned} \tag{7}$$

The Lieb-Oxford bound is satisfied[18] when $A+B\leq 1.757$ for any value of *x* or *s* (here the optimized Lieb-Oxford bound[19] by Chan and Handy is taken instead of the value of 1.804 as used in PBE), which is used to constrain the value of *B*. In principle, one could choose to constrain *D* also to give $D=E^2$, in similar fashion as the correlation part of PBE where *G* and G^2 are used, but preliminary studies showed that this destroyed the good performance. Hence, there are in total six parameters to be optimized for the (CAM-)S12g/S12h functionals (compared to eight for SSB-D): *A*, *C*, *D*, *E*, S_8, $S_{r,6}$. The latter two are needed for the D_3 dispersion contribution, so in fact there are only four parameters for the exchange-correlation part. It should be noted that for the hybrid functional a value of 0.25 is chosen for a_x (based on the non-empirical considerations by Perdew and co-workers[20]) and b_x is constrained to be equal to $1-a_x$. As mentioned above, for the CAM[13] versions three additional parameters (α, β, μ) are needed, one of which (α) is in fact equal to a_x (and constrained[20] to a value of 0.25).

III. PARAMETER OPTIMIZATION

Similarly as was done for SSB-D,[6] the parameters were optimized against a number of sets with different interactions, for which either high-level *ab initio* or experimental data are available. In comparison with the parameterization of SSB-D,[6] a number of changes have been made: the AE6 set[21] is used for atomization energies of small molecules instead of the full G2-1 set, the related BH6 set[21] for barriers of hydrogen abstraction is added, and the atomic exchange[22] of helium, neon and argon has been added for probing atomic exchange. Note that in the latter case of the NGX set, the exchange energy is obtained from a calculation where the full functional (including the correlation part) is used in the SCF; therefore the NGX value is found to be different between e.g. BP86[22,23] and BLYP,[22,24] even though both use the Becke88[22] exchange functional. Furthermore, the atomic exchange NGX set is given a low weight to avoid it from dominating completely the overall performance (TOTAL); a value of 0.05 was found to be sufficient to give good behavior of the new functionals for it. Although it would be interesting to include response properties (excitation energies, NMR chemical shifts) in the procedure for the parameters, here they were not added yet to stay as close as possible to the procedure used for obtaining the SSB-D parameters. Given in Table I are the different interaction types with their abbreviations and the weights used for them. All calculations were performed using locally modified versions of NWChem (6.0/6.1)[25] using a ‘fine’ grid and Ahlrichs’ def2-tzvp[26] basis set, except for the S_N2 energies and barriers for which the def2-qzvp[26] basis was used.

TABLE I. Interaction types taken into account for obtaining the parameters of the new functionals

	Interaction	Weight	Reference
AE6	Atomization energies of six representative molecules	1.0	[21]
BH6	Barrier heights of six hydrogen transfer reactions	3.0	[21]
FER	Metal-ring distance in ferrocene	2.0	[27]
HAL	Metal-halogen distances	1.0	[28]
NGX	Atomic exchange for He, Ne, Ar	0.05	[22]
SMLL	Accuracy of geometry for set of small molecules	2.0	[29]
SN2E	S_N2 energetics (PE from ref. [30] for reactions A2-A6)	3.0	[30]
SN2B	S_N2 barriers (for reactions A2-A6 in ref. [30])	3.0	[30]
STCK	π-π stacking in antiparallel cytosine dimer	1.0	[31]

WANG	HOH angle in water molecule	1.0	
WBND	OH bond in water molecule	2.0	
WEAK	Hydrogen-bonding in four dimers	3.0	[32]

The parameters for the new functionals are given in Table II, after optimizing to give the best results for the different interaction types from Table I. It is interesting to see that the *A* parameter is much smaller than in SSB-D; this parameter determines the behavior for x=0 (LDA limit). In principle, if a functional should be applicable to systems both in physics and chemistry, it should satisfy the LDA limit of *A*=1, which none of the popular functionals in chemistry does. It is however encouraging that the deviation from the LDA limit is almost halved, from a value of ca. 1.08 for SSB-D to ca. 1.038 for S12g. Moreover, the *C* parameter of S12g of ca. 0.0040 is very close to the one of PBE (0.0045), as are the S_8 and $S_{r,6}$ parameters for dispersion (0.722 and 1.217 for PBE, 0.844 and 1.178 for S12g). Hence, similar to SSB-D, the S12g functional is only a small correction to the non-empirical PBE.

TABLE II. Parameters for S12g, S12h, CAM-S12g and CAM-S12h

	S12g	S12h	CAM-S12g	CAM-S12h
A	1.03842032	1.02543951	1.03323556	1.02149642
C	0.00403198	0.00761554	0.00417251	0.00825905
D	0.00104596	0.00211063	0.00115216	0.00235804
E	0.00594635	0.00604672	0.00706184	0.00654977
$S_{r,6}$	1.17755954	1.07735222	1.20250451	1.08034183
S_8	0.84432515	0.37705816	0.86124355	0.37999939
a_x[a]	0	0.25	0	0.25
β	-	-	0.34485046	0.10897845
μ	-	-	1.52420731	0.48516891

a) the α parameter in the CAM functionals is equal to a_x

The parameters change quite a bit when going to the S12h functional, where the *C* and *D* parameters are almost twice as large as the values for S12g, even though the *E* parameter hardly changes. At the same time, the *A* parameter reduces even more to 1.025, but of course at the same time 25% of the exchange energy no longer comes from a pure exchange

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functional (but is instead represented by Hartree-Fock exchange). It is interesting to note that the S_8 parameter of S12h goes down to ca. 0.377, which might indicate that the short-range dispersion is better represented in S12h. Whether this is related to the doubling of the C and D parameters in S12h compared to S12g, is not certain. The parameters for the CAM-functionals are rather similar to those of S12g and S12h, e.g. the C parameter in CAM-S12g differs very little from that in S12g, and the same is seen for CAM-S12h versus S12h. In both cases of CAM-S12g and CAM-S12h does the sum of α and β add up to ca. 0.34-0.36, which is substantially lower than the value of 0.65 found in CAM-B3LYP.[13] At the same time, the μ parameter is rather large for CAM-S12g (ca. 1.52), while the value for CAM-S12h (0.485) comes close to the 0.47 value[16] advocated by Hirao and co-workers.

IV. PERFORMANCE OF THE DENSITY FUNCTIONALS

The results of the new functionals for the different interaction types of Table I are given in Table III, together with the results of several other functionals (B3LYP,[33] B3PW91,[10] B97-D,[8] BLYP,[22,24] BP86,[22,23] CAM-B3LYP,[13] KT1,[34] KT2,[34] LC-BLYP,[12] LC-PBE,[16] LC-ωPBE,[14] LDA, M06,[35] M06-2X,[35] M06-L,[36] mPW1K,[37] OLYP,[24,38] OPBE,[18,38] PBE,[18] PBE0,[20,39,40] PW6B95,[41] PW91,[42] revPBE,[43] SSB-D,[6] TPSS,[44] TPSSh;[45] including several DFT-D_3 versions of these). The choice of which functionals to include was based in part on the DFT2012 popularity poll (www.marcelswart.eu/dft-poll), from which the fifteen most popular functionals were included (apart from B2PLYP[46] that could not be included due to technical issues). The functionals are ordered according to the overall (TOTAL) deviation from the reference data, in which the weights of Table I are taken into account. It is very comforting to see that three of the new functionals belong to the four best performing functionals for these interactions, together with the M06 functional. This is even more pleasing given the low number of variables used in the design of the new functionals (four for the density functional part, plus two for the dispersion contribution; with an additional two for the CAM functionals).

Also given in Table III are the electronic energies for water at the experimental geometry, using the pcS-4 basis set. This clearly shows the problem with SSB-D as brought forward by Goerigk and Grimme,[8] leading to a large error for atomic exchange for it (NGX value 519.3 kcal·mol^{-1}). Inspecting the water energies for other functionals immediately brings forward what is the cause of this discrepancy: the KT1 and KT2 functionals[34] show electronic energies for water that are even much lower than SSB-D (respectively 0.21 and 0.52 Hartree lower). Since KT1 is included with a factor 0.358830 in SSB-D (and corrected for by another term in the exchange part of SSB-D, so in principle no double-counting should occur), this is the most likely cause for the low electronic energy of water with SSB-D. None of the new functionals described here contain a portion of KT1, therefore the electronic energy for water are now back to normal with values between -76.43 and -76.46 Hartree for (CAM-)S12g/h (and close to the CCSD(T) value of -76.43 Hartree). Also the atomic exchange is now well represented with NGX values between 5.7 and 10.8 kcal·mol^{-1}. However, this is not that surprising because of the inclusion of the NGX set in the optimization process (albeit with a low weight). Because of the poor performance of SSB-D[6] for atomic exchange, the overall (TOTAL) deviation of it (105.0) is much larger than that of its new GGA counterpart here (S12g) with a TOTAL value of 83.0. If the NGX value would not have been taken into account, SSB-D would in fact be slightly better (79.1 for SSB-D versus 82.7 for S12g).

The inclusion of a portion of Hartree-Fock exchange (25%) in S12h makes that a number of interactions are much better described. Not surprisingly, this holds for the description of barriers and atomization energies (which was already known from other studies), but also for the four hydrogen-bonded dimers (WEAK) and the metal-ring distance in ferrocene. Without any doubt the inclusion of Grimme's D$_3$ dispersion model helps in this respect, since the value of B3LYP for the hydrogen-bonded dimers (WEAK, 1.93 pm) goes down to 0.91 pm (B3LYP-D$_3$). Nevertheless, both S12g and S12h use the D$_3$ model, so there must be something else happening. Moreover, adding D$_3$ dispersion to PBE or PBE0 actually makes the performance for the hydrogen-bonding dimers worse. Some part of the better performance of S12h may also be coming from the inclusion of HF exchange, since also the hybrid PBE0 gives a slightly better performance (2.17 pm) than its GGA counterpart PBE (2.48 pm).

TABLE III. Performance[a] of several density functionals for the interaction types of Table I, indicated in **bold** are the new functionals

	AE6	BH6	FER	HAL	NGX	SMLL	SN2E
CAM-S12h	**5.81**	**2.64**	**1.13**	**1.12**	**7.57**	**1.07**	**0.65**
S12h	**6.55**	**3.55**	**1.22**	**1.14**	**6.21**	**0.96**	**0.98**
M06	3.05	1.57	0.98	1.32	60.52	1.11	1.17
CAM-S12g	**7.28**	**1.82**	**1.20**	**1.34**	**10.80**	**1.37**	**0.85**
CAM-B3LYP	2.00	3.85	0.72	1.06	51.64	0.99	1.13
mPW1K	11.98	1.52	0.42	1.35	3.80	1.67	0.80
M06-2X	1.62	1.17	8.00	3.30	45.04	1.15	1.16
PW6B95	1.89	3.50	0.40	1.17	95.35	0.93	1.68
M06-L	3.68	4.22	3.21	0.63	43.79	0.58	1.85
PBE0-D3	5.54	4.90	1.25	1.15	45.01	0.99	1.96
PBE0	5.05	4.60	0.91	1.14	45.01	0.98	1.64
B3LYP-D3	3.07	5.29	1.55	1.22	67.26	0.62	2.90
LC-ωPBE	6.90	3.96	2.97	1.58	46.96	0.95	1.34
B3LYP	3.90	4.78	2.31	1.56	67.26	0.62	2.36
TPSSh	6.49	6.65	1.35	1.10	14.94	0.55	3.46
B97-D3	2.62	6.53	0.65	1.05	59.33	0.77	4.27
S12g	**22.21**	**8.23**	**2.64**	**0.90**	**5.68**	**0.84**	**2.75**
B3PW91	22.09	5.82	1.39	1.52	62.21	0.91	1.98
BLYP-D3	6.14	8.54	2.00	1.33	9.88	1.25	4.89
TPSS	5.09	8.22	1.29	0.75	16.12	0.78	4.53
sPBE	10.73	8.79	0.09	0.72	60.97	1.05	4.05
BP86	11.91	9.32	0.34	0.93	9.22	1.01	3.90
BP86-D3	13.12	9.91	1.04	0.98	9.22	1.02	4.57
PBE-D3	14.67	9.61	1.21	0.86	60.96	1.00	4.50
LC-PBE47	13.81	3.24	5.78	2.81	143.15	1.80	2.38
PBE	14.21	9.32	0.94	0.85	60.96	0.99	4.16
LC-BLYP	18.43	7.49	2.76	2.41	107.43	1.18	1.64
BLYP	6.93	7.91	2.91	1.39	9.88	1.23	4.16
revPBE	8.95	6.61	0.30	1.13	17.75	1.18	3.20
PW91	14.69	9.58	0.82	0.96	20.39	0.88	4.55

SSB-D	22.88	7.34	4.73	1.03	519.27	0.61	2.34
OLYP	4.19	6.06	1.07	1.27	6.13	0.76	2.10
LC-PBE	28.15	8.46	5.71	3.58	143.15	1.38	1.49
OsPBE	6.93	5.17	3.63	1.04	8.51	0.95	1.71
OPBE	10.19	5.75	4.45	1.30	8.80	1.01	1.75
KT1	26.09	14.12	0.62	1.62	480.48	1.41	7.88
KT2	7.42	12.25	2.70	3.00	1093.94	0.35	7.39
LDA	75.73	18.28	5.35	3.47	762.60	1.37	5.87

TABLE III (contd.). Performance^a of several density functionals for the interaction types of Table I, indicated in **bold** are the new functionals

	SN2B	STCK	WANG	WBND	WEAK	TOTAL	E(water)^b
CAM-S12h	**0.33**	**0.58**	**0.54**	**0.07**	**1.03**	**26.90**	**-76.457**
S12h	**0.65**	**0.38**	**0.32**	**0.00**	**1.20**	**32.20**	**-76.453**
M06	1.08	1.78	0.65	0.09	2.88	34.28	-76.435
CAM-S12g	**1.30**	**0.32**	**0.69**	**0.44**	**2.19**	**34.66**	**-76.431**
CAM-B3LYP	1.10	6.20	1.19	0.34	2.06	41.55	-76.446
mPW1K	0.79	7.32	1.08	0.62	1.82	42.13	-76.442
M06-2X	0.93	0.31	1.01	0.25	2.60	44.86	-76.438
PW6B95	2.17	4.40	0.74	0.03	2.41	44.95	-76.551
M06-L	2.38	1.56	0.41	0.26	2.72	50.11	-76.456
PBE0-D3	2.23	0.63	0.55	0.20	2.67	50.28	-76.388
PBE0	2.31	6.54	0.55	0.20	2.17	51.88	-76.388
B3LYP-D3	3.71	0.04	0.74	0.51	0.91	52.21	-76.474
LC-ωPBE	1.37	6.88	0.53	0.73	2.46	54.93	-76.413
B3LYP	3.83	8.56	0.73	0.51	1.93	63.71	-76.474
TPSSh	5.68	8.36	0.24	0.70	1.46	73.89	-76.466
B97-D3	6.22	1.18	0.04	0.82	3.73	74.56	-76.433
S12g	**3.42**	**0.00**	**0.64**	**0.84**	**2.38**	**83.00**	**-76.460**
B3PW91	3.29	7.97	0.68	0.06	4.02	85.41	-76.605
BLYP-D3	6.94	0.30	0.04	1.54	2.48	86.42	-76.458
TPSS	7.40	8.69	0.06	1.16	1.38	86.49	-76.475
sPBE	6.25	7.05	0.22	1.38	1.19	87.63	-76.424
BP86	6.82	9.46	0.13	1.37	2.09	94.69	-76.478
BP86-D3	6.61	0.56	0.12	1.37	3.21	95.01	-76.478
PBE-D3	6.33	0.96	0.23	1.35	2.96	97.06	-76.388
LC-PBE47	3.71	4.41	1.85	0.14	8.21	98.10	-76.280
PBE	6.42	6.96	0.23	1.35	2.48	98.98	-76.388
LC-BLYP	1.22	2.28	1.34	0.98	9.47	99.13	-76.325
BLYP	7.20	10.29	0.03	1.54	4.11	100.61	-76.458
revPBE	5.86	11.01	0.50	1.39	8.48	100.69	-76.448
PW91	6.76	6.48	0.07	1.22	3.72	102.88	-76.447
SSB-D	2.63	0.11	1.15	0.11	2.02	105.02	-77.005
OLYP	3.99	14.07	0.54	0.83	20.29	123.01	-76.451
LC-PBE	1.30	3.27	0.85	0.93	13.73	133.97	-76.276
OsPBE	2.87	15.18	0.77	0.59	25.81	141.34	-76.472
OPBE	3.05	15.25	0.77	0.54	23.59	142.36	-76.439
KT1	10.11	0.80	1.19	1.51	15.05	202.26	-77.211
KT2	9.38	0.92	0.72	0.26	18.40	215.61	-77.516
LDA	6.96	0.35	0.75	1.38	20.27	288.75	-75.913

a) given are the deviations from the reference data, either in kcal·mol^{-1} for energies, degrees for angles or pm for distances;

b) total electronic energy of water using the pcS-4 basis set, using experimental geometry (OH 0.957 Å, HOH 104.5°)

As already noted before, the simplification of the correlation part in sPBE makes that hydrogen-bonding is described better in it than in PBE. This again shows up here with deviations of 1.19 pm (sPBE) and 2.48 pm (PBE) for the WEAK set. Overall, the simplified

PBE (sPBE) functional shows smaller deviations (87.6 versus 99.0 for PBE) as well. However, this is mostly limited to the combination with PBE exchange; in combination with the OPTX functional the TOTAL values are almost identical (141.3 for OsPBE versus 142.3 for OPBE).

The barriers for the S_N2 reaction[30] are best described by either CAM-S12h or S12h, with deviations from the (CCSD(T)) reference data of only 0.3-0.7 kcal·mol^{-1}, although also mPW1K (deviation 0.8 kcal·mol^{-1}), M06-2X (0.9 kcal·mol^{-1}) or M06 (1.1 kcal·mol^{-1}) give good results. On the other hand, these latter functionals work better for the hydrogen-abstraction reactions of the BH6 set[21] with deviations of 1.2 kcal·mol^{-1} (M06-2X), 1.5 kcal·mol^{-1} (mPW1K) and 1.6 kcal·mol^{-1} (M06). The values of CAM-S12g (1.8 kcal·mol^{-1}), CAM-S12h (2.6 kcal·mol^{-1}) and S12h (3.5 kcal·mol^{-1}) are substantially larger, but are still a major improvement over the values for other functionals. This is in particular true for GGA functionals like S12g (deviation BH6 8.2 kcal·mol^{-1}), SSB-D (7.3 kcal·mol^{-1}), OPBE (5.8 kcal·mol^{-1}) or BP86 (9.3 kcal·mol^{-1}). It should be noted therefore that although the barrier for S_N2 reactions can be better described by a small adjustment of a GGA in the region of $s<1$, this is not true for the hydrogen-abstraction reactions.

V. SPIN STATE ENERGIES

One of the main challenges for density functionals is posed by spin state energies,[47,48] and therefore the new functionals are also checked for their spin-state splittings of monopyridylmethylamine Fe(II)(amp)$_2$Cl$_2$ and dipyridylmethylamine Fe(II)(dpa)$_2^{2+}$. These two related iron complexes pose a severe check on computational methods,[49] given that the former has a high-spin ground state and the latter a low-spin. Given in Table IV are the spin state energies for the set of density functionals.

TABLE IV. Spin state energies for Fe(II)(amp)$_2$Cl$_2$ and Fe(II)(dpa)$_2^{2+}$ of several density functionals, indicated in **bold** are those functionals that predict both spin states correctly

	Fe(II)(amp)$_2$Cl$_2$ (h.s.[a])		Fe(II)(dpa)$_2^{2+}$ (l.s.[b])	
	S=0	S=2	S=0	S=2
CAM-S12h	25.15	0	12.80	0
S12h	31.00	0	11.75	0
M06	25.30	0	10.71	0
CAM-S12g	38.12	0	22.43	0
CAM-B3LYP	18.14	0	3.85	0
mPW1K	36.69	0	23.05	0
M06-2X	49.11	0	32.52	0
PW6B95	16.26	0	1.15	0
M06-L	9.40	0	0	5.03
PBE0-D3	20.42	0	5.11	0
PBE0	21.29	0	7.64	0
B3LYP-D3	16.03	0	0	0.06
LC-ωPBE	7.79	0	0	6.76
B3LYP	17.54	0	4.23	0
TPSSh	2.82	0	0	10.78
B97-D3	11.09	0	0	4.88
S12g	5.79	0	0	9.35
B3PW91	47.83	0	36.82	0
BLYP-D3	0	4.97	0	22.01
TPSS	0	9.91	0	23.53
sPBE	0	5.05	0	18.30
BP86	0	8.49	0	22.11
BP86-D3	0	10.07	0	27.19
PBE-D3	0	9.51	0	24.65
LC-PBE47	8.65	0	0	7.15
PBE	0	8.82	0	22.41
LC-BLYP	0	4.11	0	20.04
BLYP	0	3.21	0	16.22
revPBE	0.54	0	0	11.67
PW91	0	10.69	0	24.26
SSB-D	10.56	0	0	7.65
OLYP	11.69	0	0.79	0
LC-PBE	0	10.28	0	26.67
OsPBE	11.40	0	0.85	0
OPBE	7.49	0	0	3.28
KT1	0	27.11	0	43.10
KT2	0	19.25	0	35.28
LDA	0	37.12	0	55.52

a) high-spin (S=2) experimentally; b) low-spin (S=0) experimentally

Despite the good performance for the other interactions (see Table III), the new hybrid functionals (S12h, CAM-S12g, CAM-S12h) are unable to correctly predict the spin-state for the low-spin compound Fe(II)(dpa)$_2^{2+}$, like almost all hybrid functionals. There are however three exceptions: TPSSh, LC-PBE47 and LC-ωPBE (see Table IV), which together with

OPBE, SSB-D, S12g, M06-L and B97-D3 make up the set of "reliable" density functionals for spin-state splittings (at least for the two challenging iron-complexes studied here). The good performance of TPSSh was already reported in the literature before,[50] and most likely results from the limited amount of HF exchange included in it (10%). Surprisingly enough, the two other hybrid functionals that work well contain 100% (long-range) HF exchange, but nevertheless work well for these spin state energies. This is a feature that might be explored in future studies as a way forward for obtaining both accurate thermochemistry for organic molecules (hybrid functionals) and at the same time correct spin-state splittings. On the other hand, it is comforting to see that S12g retains the good performance of SSB-D for spin-state energies.

VI. CONCLUSIONS

A new family of (range-separated) hybrid density functionals is presented that includes Grimme's D_3 dispersion contribution. The parameters for these functionals are optimized against a number of different interaction types, leading finally to four functionals. The hybrid functional S12h and its range-separated analogue CAM-S12h are the best performing density functionals for these interaction types when compared with the most popular density functionals in use in current chemical research. A more extensive comparison for other databases (e.g. by Grimme or Truhlar) will be published elsewhere. Based on the reduced computational demand of S12h versus CAM-S12h (less than half), there is a slight preference for S12h in everyday use. However, it should be noted that neither one of the new hybrid functionals should be used for spin-state splittings, because of their preference for high-spin states due to the inclusion of HF-exchange. For spin-states, S12g would be a reliable alternative.

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