Effectiveness of Diffuse Basis Functions for Calculating Relative Energies by Density Functional Theory

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The addition of diffuse functions to a double-ζ basis set is shown to be more important than increasing to a triple-ζ basis when calculating reaction energies, reaction barrier heights, and conformational energies with density functional theory, in particular with the modified Perdew−Wang density functional. It is shown that diffuse basis functions are vital to describe the relative energies between reactants, products, and transition states in isogyric reactions, and they provide enormous improvement in accuracy for conformational equilibria, using 1, 2-ethanediol and butadiene as examples. As a byproduct of the present study, we present a one-parameter hybrid density functional method optimized for sugars and sugar-like molecules; this is called MPW1S.

1. Introduction

The parameters in the 6-31G Gaussian basis set[1,2] were found by minimizing the Hartree−Fock[3] (HF) energies of atoms. Similarly, the parameters of the 6-311G basis[4,5] were chosen to minimize atomic energies at the second-order Møller−Plesset (MP2) correlated level of theory.[6] Anions have a more spread out electron density than neutral atoms, so diffuse functions must be added to treat them properly. For both of the 6-31G and 6-311G basis sets, as well as other basis sets in the literature, diffuse functions have been designed to minimize the energy of small anions.[7−9]

The basis sets mentioned above are now widely used for density functional theory[10] (DFT) and hybrid Hartree−Fock density functional theory[11] (HDFT). Hybrid DFT, based on the adiabatic connection formula,[11] incorporates a nonlocal exchange-correlation hole by an empirical mixing of Hartree−Fock and gradient-corrected density-based exchange and has proved to be a powerful technique for quantitative modeling.[12] Although there was a widespread hope that DFT and HDFT should require smaller basis sets than explicitly correlated methods such as MP2, configuration interaction, and coupled cluster theory, careful tests[13] have shown that actual convergence with respect to the basis set size can be slow with density-based methods too. Our own experience has indicated that the effectiveness of various kinds of basis functions that might be added to extend a basis set is quite different in wave function-based theories and density-based theories. In particular, we have found that diffuse functions are much more important for calculating relative energies that do not involve bond breaking in density-functional calculations than they are in traditional SCF theories. Furthermore, our reading of the literature has convinced us that this is not as widely appreciated as it should be. Therefore, in the present paper, we document some of the experience that has led us to this conclusion. In particular, we will examine the accuracy of the mPW1PW91[14] and MPW1K[15] hybrid density functional methods with valence double-ζ[1,2,5] and valence triple-ζ[4,5,16,17] basis sets, with and without diffuse functions, for

calculating atomization energies (AEs), reaction barrier heights (BHs), energies of reaction (ΔEs), electron affinities (EAs), ionization potentials (IPs), and conformational energies (CEs). Section 2 defines the theoretical methods used. Section 3 describes the results.

2. Methods

We introduce two new basis sets to use in our calculations. They are both derived from the MG3 basis,[16,17] which is identical to 6-311++G(2df,2p)[4,5,7,8] for first-row elements and hydrogen, identical to 6-311+G(3d2f)[7,8,18] for sodium, magnesium, aluminum, and silicon, and very similar to 6-311+G(3d2f) [7,8,18] for phosphorus, sulfur, and chlorine. The first new basis is the MG3 semi-diffuse (MG3S) basis which is identical to MG3 except that the diffuse functions on hydrogen have been removed. The second basis set is the MG3 tight (MG3T) basis, which removes all diffuse functions from the MG3 basis; thus the MG3T basis is a polarized valence triple-ζ basis with no diffuse functions. We also use the previously existing 6-31G-(d,p)[1,2,5,8] and 6-31+G(d,p)[1,2,5,7,8] basis sets.

To investigate the importance of diffuse functions, we compare calculated and experimental AEs, BHs, IPs, EAs, ΔEs, and CEs.

Our atomization energy database is constructed by merging our original 82-molecule set[19] with another 27 molecules selected later.[20] The zero-point-exclusive atomization energies (D_e) for all but seven of the molecules are identical to those previously published.[19,20] For the present work, more accurate experimental and theoretical data were used to reevaluate D_e for CH_3,[21] $CH_2(^3B_1)$,[21] $CH_2(^1A_1)$,[21] H_2CCO,[21] H_2,[22] OH,[23] and H_2O.[23] The merged and updated D_e database is given in Table 1. This table also corrects a typo in the value of D_e for Si_2 in ref 19, and it corrects errors in the zero-point energies of the methylene species in ref 19.

For barrier heights and energies of isogyric reactions, we use 44 zero-point-exclusive barrier heights and 22 zero-point-exclusive ΔEs from a previously published kinetics database.[24]

For IPs and EAs, we chose the six atoms and seven molecules for which the IP and EA are both present in the G3[25] data set.

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TABLE 1: Zero-Point-Exclusive Atomization Energies (kcal/mol)

molecule	D_e	molecule	D_e	molecule	D_e
$CH(_2\Pi)$	84.00	S_2	101.67	H_2CCH	445.79
$CH_2(^3B_1)$	190.97	Cl_2	57.97	$HCOOOCH_3$	785.26
$CH_2(^2A_1)$	181.50	SiO	192.08	HCOOH	500.98
$CH_3(^2A''_2)$	307.46	SC	171.31	NF_3	204.53
CH_4	420.11	SO	125.00	PF_3	363.87
NH	83.67	ClO	64.49	SH	86.98
NH_2	181.90	ClF	61.36	$SiCl_4$	384.94
NH_3	297.90	Si_2H_6	530.81	SiF_4	574.35
OH	107.06	CH_3Cl	394.64	C_2H_5	603.75
OH_2	232.60	CH_3SH	473.84	$C_4H_6{}^d$	987.2
FH	141.05	HOCl	164.36	$C_4H_6{}^e$	1001.61
SiH_2 ($^1A_1$)	151.79	SO_2	257.86	HCOCOH	633.35
SiH_2 ($^3B_1$)	131.05	$AlCl_3$	306.26	CH_3CHO	677.03
SiH_3	227.37	AlF_3	426.50	C_2H_4O	650.70
SiH_4	322.40	BCl_3	322.90	C_2H_5O	698.64
PH_2	153.20	BF_3	470.04	H_3CCH_2OH	798.05
PH_3	242.55	C_2Cl_4	466.28	H_3CCH_2OH	810.36
SH_2	182.74	C_2F_4	583.96	$C_3H_4{}^f$	703.20
ClH	106.50	$C_3H_4{}^a$	704.79	$C_3H_4{}^g$	682.74
HCCH	405.39	C_4H_4O	993.74	H_3CCOOH	803.04
H_2CCH_2	563.47	C_4H_4S	962.73	H_3CCOCH_3	977.96
H_3CCH_3	712.80	C_4H_5N	1071.57	C_3H_6	853.41
CN	180.58	$C_4H_6{}^b$	1012.37	H_3CCHCH_2	860.61
HCN	313.20	$C_4H_6{}^c$	1004.13	C_3H_8	1006.87
CO	259.31	C_5H_5N	1237.69	$C_2H_5OCH_3$	1095.12
HCO	278.39	CCH	267.83	$C_4H_{10}{}^h$	1303.04
H_2CO	373.73	CCl_4	312.74	$C_4H_{10}{}^i$	1301.32
H_3COH	512.78	CF_3CN	639.85	$C_4H_8{}^j$	1149.01
N_2	228.46	CF_4	476.32	$C_4H_8{}^k$	1158.61
H_2NNH_2	228.46	CH_2OH	409.76	$C_5H_8{}^l$	1284.28
NO	155.22	CH_3CN	615.84	C_6H_6	1367.56
O_2	119.99	CH_3NH_2	582.56	CH_3CO	581.58
HOOH	268.57	CH_3NO_2	601.27	$(CH_3)_2CH$	900.75
F_2	38.20	$CHCl_3$	343.18	$(CH_3)_3C$	1199.34
CO_2	389.14	CHF_3	457.50	H_2CCO	532.73
Si_2	74.97	ClF_3	125.33		
P_2	117.09	H_2	109.48		

[a] Propyne. [b] *trans*-1,3-Butadiene. [c] 2-Butyne. [d] Bicyclobutane. [e] Cyclobutane. [f] Allene. [g] Cyclopropene. [h] Cyclobutene. [i] Isobutene. [j] Transbutane. [k] Isobutene. [l] Spiropentane.

TABLE 2: Zero-Point-Exclusive Ionization Potentials and Electron Affinities (kcal/mol)

	IP	EA		IP	EA		IP	EA
C	259.7	29.1	OH	299.1	42.1	PH_2	226.3	29.4
S	238.9	47.9	O	313.9	33.7	S_2	216.0	38.5
SH	238.9	53.3	O_2	278.9	10.8	Si	187.9	32.0
Cl	299.1	83.3	P	241.9	17.2			
Cl_2	265.3	55.6	PH	234.1	23.2			

For convenience, we convert all IPs and EAs to zero-point exclusive EAs and IPs which can be directly compared to calculated results. The zero-point energies needed for this conversion are calculated using mPW1PW91/MG3 frequencies scaled by 0.9758 and removed from the experimental values. The scaling factor of 0.9758 was obtained by minimizing the root-mean-squared error (RMSE) over the database[26] of ZPEs developed in a previous paper. The zero-point exclusive EAs and IPs are listed in Table 2.

The CEs consist of theoretical data[27] for 1,2-ethanediol and experimental data[28] for butadiene. For 1,2-ethandiol, the data consists of the relative CEs of all 45 possible pairs of all 10 conformations as computed by a composite method[27] based on MP2/cc-pVTZ and CCSD(T)/cc-pVDZ energies at MP2/cc-pVDZ geometries. For butadiene, the data consists of relative CEs of all six possible pairs of both conformations and both transition states.[28]

TABLE 3: Mean Signed Errors (MSE) and Mean Unsigned Errors (MUE) (kcal/mol) for mPW1PW91 Methods

		no. of data	6-31G(d,p)	6-31+G(d,p)	MG3T	MG3S
AE[a]	MSE	109	−3.6	−7.2	−2.2	−3.4
	MUE		6.6	7.5	3.7	4.2
BH[b]	MSE	44	−4.6	−4.0	−4.3	−3.8
	MUE		4.6	4.0	4.3	3.8
IP[c]	MSE	13	2.8	4.0	2.5	3.2
	MUE		3.4	4.0	3.3	3.7
EA[d]	MSE	13	−16.1	0.1	−11.7	−1.1
	MUE		17.1	2.8	11.9	2.6
DE[e]	MUE	22	2.3	1.2	1.4	1.2
CE[f]	MUE	6[g]	0.84	0.67	0.69	0.65

[a] Atomization energies. [b] Barrier heights. [c] Ionization potentials. [d] Electron affinities. [e] Reaction energies for isogyric reactions. [f] Conformational energies. [g] Butadiene.

TABLE 4: Mean Signed Errors (MSE) and Mean Unsigned Errors (MUE) (kcal/mol) MPW1K Methods

		no. of data	6-31G(d,p)	6-31+G(d,p)	MG3T	MG3S
AE[a]	MSE	109	−12.1	−14.9	−10.2	−10.9
	MUE		12.5	14.9	10.3	11.0
BH[b]	MSE	44	−1.6	−1.1	−1.4	−1.0
	MUE		2.1	1.7	1.8	1.7
IP[c]	MSE	13	3.5	4.3	3.0	3.4
	MUE		4.3	4.5	3.6	3.5
EA[d]	MSE	13	−15.7	−1.5	−12.1	−2.8
	MUE		16.9	4.1	12.4	3.7
DE[e]	MUE	22	3.0	1.6	1.9	1.3
CE[f]	MUE	6[g]	0.64	0.51	0.55	0.53

[a] Atomization energies. [b] Barrier heights. [c] Ionization potentials. [d] Electron affinities. [e] Reaction energies for isogyric reactions. [f] Conformational energies. [g] Butadiene.

In comparing our new calculations to the test data, we used the following geometries: For 1,2-ethanediol, we used MP2/cc-pVDZ geometries from ref 27. For butadiene, all geometries were optimized at the level tested. For all other cases, we used QCISD/MG3 geometries calculated for the present work, where QCISD denotes quadratic configuration interaction with single and double excitations.[29]

All calculations were performed with the Gaussian 98 electronic structure package.[30] The spin−orbit coupling[26] was added to all atoms and open-shell molecules for which it is nonzero. However, it was neglected for transition states, which is reasonable[31] because they typically have no low-lying excited electronic states.

3. Results and Discussion

Table 3 shows mean signed errors (MSE) and mean unsigned errors (MUE) for mPW1PW91 with each of the four basis sets. Table 4 lists the same information for MPW1K.

Consider first the atomization energies, which involve bond breaking. Tables 3 and 4 show that omitting the diffuse functions leads to a cancellation of errors for the atomization energies. For both methods, when diffuse functions are added, the MUE increases. This can be explained by the diffuse functions tending to stabilize the atoms more than the molecules.

In contrast to the above trends for absolute atomization energies, the 6-31+G(d,p) basis outperforms the MG3T basis for BHs, EAs, ΔEs, and butadiene CEs when using either the mPW1PW91 or MPW1K hybrid density functional methods. Not surprisingly, EAs show the most dramatic improvement when diffuse functions are added. Using mPW1PW91, the diffuse functions added to the 6-31G(d,p) basis reduce the error

TABLE 5: Mean Unsigned Errors (kcal/mol) for Conformational Energies of Butadiene

	6-31G(d,p)	6-31+G(d,p)	MG3T	MG3S
mPW1PW91	0.84	0.67	0.69	0.65
MPW1K	0.64	0.51	0.55	0.53
average[a]	0.74	0.59	0.62	0.59
MP2	0.29	0.20	0.45	0.41
MP3	0.29	0.37	0.29	0.25
average[a]	0.29	0.29	0.37	0.33

[a] Average of mPW1PW91 and MPW1K. [b] Average of MP2 and MP3.

TABLE 6: Mean Unsigned Errors (kcal/mol) in 45 Relative Conformational Energies of 1,2-Ethanediol

	6-31G(d,p)	6-31+G(d,p)
HF	0.49	0.70
mPW1PW91[a]	0.39	0.17
MPW1K[b]	0.29	0.26
MPW1S[c]	0.55	0.09
MPW0[d]	0.62	0.11
Average[e]	0.46	0.16

[a] Same as MPW25. [b] Same as MPW42.8. [c] Same as MPW6. [d] Same as mPW1PW91. [e] Average of four mPW and MPW methods.

by 84%, but going to the much larger MG3S basis reduces the error by only a modest 7% as compared to the 6-31+G(d,p) basis. IPs are not systematically improved when diffuse functions are added.

Isogyric reactions are reactions in which the number of unpaired electrons does not change, and hence, the number of electron pairs does not change either.[32] All 22 reactions in our test set are isogyric atom-transfer reactions. It is especially interesting to contrast the performance of diffuse functions for AEs and Δ*E*s. Although adding diffuse functions gives worse results for AEs, they improve isogyric Δ*E*s. We interpret this as follows: the good performance of tight basis sets (i.e., basis sets without diffuse functions) results from a cancellation of the large systematic errors in bond dissociation energies. However, this cancellation does not occur in atom-transfer reactions. In such a case, the improvement in the diffuse part of the basis set is required in order to have a basis set that is better balanced for different kinds of bonds.

The improvement afforded by diffuse functions on butadiene conformations is particularly notable. The last rows of Tables 3 and 4 show that omitting diffuse basis functions from the 6-31+G(d,p) basis increases the error by 25% for this example. The effect is smaller when we compare MG3T to MG3S, as expected because diffuse functions are less important in a triple-ζ basis. We added the butadiene case to the present paper because of the recent systematic study of Sancho-Garcia et al. which indicated[33] that torsional profiles of conjugated systems provide a key type of test problem for DFT. (As a side issue to the main subject of the present paper, i.e., diffuse functions, we note that Hartree−Fock is more accurate than DFT for this problem, although for most other chemical problems this is not true.)

Table 5 gives further comparisons for butadiene; in particular, we employed the same four basis sets for conventional wave function calculations by Møller−Plesset[6] second-order (MP2) and third-order (MP3) perturbation theory. Averaging over the two sets of density functional calculations, the addition of diffuse functions lowers the error by 23%, whereas it makes essentially no difference (on average) for the wave function calculations. Strikingly, the 6-31+G(d,p) basis with its diffuse functions outperform the triple-ζ valence MG3T basis for the density functional calculations but underperforms it for the MP3 wave function calculations. This further confirms our conclusion that diffuse functions are more important in density-based methods than in wave function methods. One should keep in mind that a considerable amount of the lore of the field was developed from experience with wave function calculations.

Finally, we consider 1,2-ethanediol (ethylene glycol), where the importance of diffuse functions is illustrated even more dramatically. There are 10 unique conformations of 1,2-ethanediol. In a previous paper, the geometries of all 10 conformations were optimized by MP2 theory with a polarized valence double-ζ basis, and accurate relative energies were calculated by single-point energy calculations with a composite method in which MP2 calculations with a polarized valance triple-ζ basis were corrected for higher-order effects by CCSD-(T) calculations.[27] All 1,2-ethanediol calculations in the present paper are single-point energy calculations at the above geometries, and the accurate relative energies from previous work are used for testing the ability of the new calculations to predict relative conformational energies. Conformational analysis is central to the prediction of chemical equilibria and reactivity, and it plays a prominent role in drug design.[34,35] The 1,2-ethanediol molecule is a good test case for conformational energy predictions because accurate calculations are available[27] for the relative energies of all 10 of its unique conformers, which span an energy range of 3.7 kcal/mol. The 1,2-ethandiol molecule is also of interest in its own right as the simplest model of a sugar and as a model compound for diols employed as the chemical core of various inhibitors of HIV-1 protease. The question of diffuse functions has been debated fiercely in the carbohydrate modeling community.

The first row of Table 6 shows that adding diffuse functions to the 6-31G(d,p) basis set considerably degrades the accuracy at the HF level, whereas the next two rows show that the opposite is true for the two hybrid DFT methods that we have used in this paper. We note that MPW1K is like mPW1PW91 except that the percentage of Hartree−Fock exchange, which we call *x*, has been increased from 25 to 42.8 ("1K" denotes 1 parameter optimized for kinetics). More generally, we denote a method of this type in which *x* is varied for the mPW exchange functional and the PW91 correlation functional as MPW*x*. We optimized *x* to minimize the error for the present problem; this yields *x* = 6. The resulting model, MPW6, is also called MPW1S, where "1S" denotes 1 parameter optimized for sugars (1,2-ethanediol is not actually a sugar, but it is reasonable to use it to optimize parameters for sugars). Table 6 shows that the effect of diffuse functions is even more dramatic for MPW1S. Finally, the last row of Table 5 shows results for a pure density functional (*x* = 0); again, diffuse functions are very powerful.

Because the diffuse functions in Table 6 become more important when the fraction of density-functional exchange increases, one might ask whether the effect of diffuse functions can be further analyzed in terms of its separate effect on exchange and correlation. However, this is complicated by the approximate cancellation between the nonlocalities of exchange and correlation,[36] and it is beyond our scope to analyze this further.

The 6-31+G(d,p) basis set that performs so admirably here is much more affordable for large carbohydrates than the extended basis sets[27,37−39] that have been used in some previous studies of sugar-like molecules.

4. Concluding Remarks

Density functional theory[10] and its first cousin, hybrid density functional theory,[11] have received wide recognition for their

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cost-efficient utility for computational thermochemistry[10−14] and computational thermochemical kinetics.[15,24,40] Hybrid DFT replaces a percentage x of the gradient-corrected DFT exchange functional by the nonlocal Hartree−Fock exchange operator. Various values of x ranging from 0 to about 50 have been proposed as optimum for various problems.

One goal of the present study was to optimize x for conformational analysis of the ethylene glycol molecule to learn whether the standard value ($x = 25^{14}$) is close to optimum for this kind of problem. Another goal was to make a broader, more systematic test of our recent assertions[15,40] that the inclusion of diffuse basis functions is critical to obtaining peak performance for balanced calculations of bond energies across a range of bond types by using hybrid DFT. The present paper does indeed confirm that assertion. In particular, the "valence double zeta plus single polarization and diffuse" basis set, 6-31+G(d,p), is more accurate than the "valence triple zeta plus multiple polarization but tight" basis set MG3T for barrier heights, energy changes in isogyric reactions, and conformational energies.

We conclude that diffuse basis functions are very important for optimizing the performance of DFT, even in a problem such as 1,2-ethandiol, where they do not improve the performance of HF theory. The importance of diffuse functions in a double-ζ basis set for calculating conformations of carbohydrates was also noted by Csonka in a recent paper.[41] We also conclude that 6% HF exchange is optimum for 1,2-ethanediol (and hence probably close to optimal for a number of conformational problems in sugar chemistry). Pure DFT with no HF exchange is only slightly less accurate for 1,2-ethanediol. The 45 energy differences among the unique conformers of 1,2-ethanediol are predicted with a mean unsigned error of only 0.09 kcal/mol, which is only 2.5% of the 3.68 kcal/mol range exhibited by the data set.

We conclude by emphasizing two critical aspects of the present conclusions. In a very general sense, there is widespread recognition that diffuse functions can be important. Our study presented here makes two more specific points, namely: (1) Diffuse functions are much more important for DFT and hybrid DFT than for Hartree−Fock. Although the electronic structure community has built a considerable amount of intuition about basis sets on experiences gained with Hartree−Fock calculations, conclusions about diffuse functions gained in that way do not carry over to DFT. (2) The mere addition of diffuse functions on nonhydrogenic atoms to a singly polarized valence double-ζ basis set often removes the bulk of the error so that many calculations employing more extended basis sets (valence triple-ζ, multiple polarization, and diffuse on H) are unnecessarily large (although MG3S is systematically better than 6-31+G(d,p)).

Considering the performance vs cost tradeoff, we recommend that diffuse functions always be included on nonhydrogenic atoms in DFT and hybrid DFT calculations unless the sole goal of the calculation is absolute bond energies or absolute ionization potentials.

Appendix

In the course of this work, we discovered an error in the modified Perdew-Wang hybrid density functional method[14] as coded in Gaussian 98.[30] This error was corrected for all calculations in the present paper. The error has only a small effect on previously published work[15,40] from our group that employ the modified Perdew−Wang functional, but the error does sometimes affect the tenths place for energies expressed in kcal/mol, and thus, it is important to document the error and its correction.

The constant A_y appears in the derivation of the local spin density approximation in DFT and is defined as

$$A_y = -\frac{3}{2}\left(\frac{3}{4\pi}\right)^{1/3} \tag{1}$$

The reduced gradient of the density ρ with spin σ is

$$y = \frac{|\nabla\rho_\sigma|}{(\rho_\sigma)^{4/3}} \tag{2}$$

The gradient-corrected enhancement factor for the mPW density functional is defined as

$$F[y] = \frac{by^2 - (b - \beta)y^2 \exp(-cy^2) - 10^{-6}y^d}{1 + 6by\sinh^{-1}y - \frac{10^{-6}y^d}{A_y}} \tag{3}$$

where b, β, c, and d are constants. The pure gradient-corrected density functional is then

$$F^{\text{pure}} = (A_y - F[y])\rho_\sigma^{1/3} \tag{4}$$

The DFT portion of the hybrid density functional introduces the scaling factors for the local and gradient-corrected portions of the exchange, $(1-x/100)$ and f_{GCF}, respectively, where x is the percentage of HF exchange. The form of the functional is then

$$F^{\text{hybrid}} = \left(\left(1 - \frac{x}{100}\right)A_y - f_{\text{GCF}}F[y]\right)\rho_\sigma^{1/3} \tag{5}$$

If we substitute $F[y]$ in eq 5 by using eq 3, we obtain the correct hybrid form for the mPW exchange energy:

$$E_y^{\text{GGA−hybrid}} = \sum_\sigma \int \left(\left(1 - \frac{x}{100}\right)A_y - f_{\text{GCF}}\frac{by^2 - (b - \beta)y^2\exp(-cy^2) - 10^{-6}y^d}{1 + 6by\sinh^{-1}y - \frac{10^{-6}y^d}{A_y}}\right)\rho_\sigma^{4/3}\,\text{d}^3r \tag{6}$$

However, the mPW energy in all versions of Gaussian 98 through the present version (Gaussian 98, revision A.11) is

evaluated using the following incorrect form

$$E_y^{\text{GGA}-\text{hybrid}} = \sum_\sigma \int \left(\left(1 - \frac{x}{100}\right)A_y - f_{\text{GCF}} \frac{by^2 - (b-\beta)y^2 \exp(-cy^2) - 10^{-6}y^d}{1 + 6by\sinh^{-1}y - \dfrac{10^{-6}y^d}{\left(1 - \dfrac{x}{100}\right)A_y}} \right) \rho_\sigma^{4/3} \, \mathrm{d}^3r \quad (7)$$

The coefficient, $(1 - x/100)$, used to scale the local density exchange has snuck its way into the denominator of the gradient corrected portion of the functional in eq 7, making the density functional itself dependent on the fraction of DFT exchange used in the hybrid method. The typical error introduced by this error is less than a 0.1 kcal/mol for energies of reaction or bond strengths.

Note that, in the present paper, we set $f_{\text{GCF}} = (1 - x/100)$, but in this appendix, we allowed for the more general case where these are not equal in order to explain the error clearly.

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