



Generalized Gradient Approximation That Recovers the Second-Order Density-Gradient Expansion with Optimized Across-the-Board Performance

Roberto Peverati,[†] Yan Zhao,[‡] and Donald G. Truhlar^{*,†}

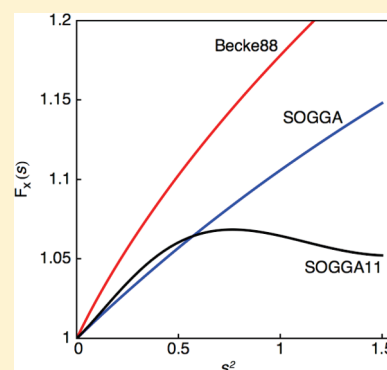
[†]Department of Chemistry and Supercomputing Institute, University of Minnesota, Minneapolis, Minnesota 55455, United States

[‡]Commercial Print Engine Lab, HP Laboratories, Hewlett-Packard Co., 1501 Page Mill Road, Palo Alto, California 94304, United States

S Supporting Information

ABSTRACT: We present a new generalized gradient approximation (GGA) to the exchange-correlation functional of density functional theory, called SOGGA11, that has better overall performance for a broad chemical database than any previously available GGA and in addition is correct to second order (SO) in the density-gradient. It provides excellent accuracy for predicting molecular bond lengths.

SECTION: Molecular Structure, Quantum Chemistry, General Theory



Density functional theory (DFT) has emerged as the preferred method for the calculation of the electronic structure, properties, and potential energy surfaces of all but the smallest chemical systems.^{1,2} The first density functional approximation proposed in the original Kohn–Sham paper³ was a function of only the electron density; such a function is generally believed to be exact only for a system with uniform density. The development of improved approximations to the exchange-correlation functional has been a crucial ingredient in the success of DFT.

The leading correction for nonuniform density comes in at second order (SO) in the density gradient, but truncation of the density expansion of the exchange functional at SO does not yield a good global approximation to the exchange hole, so it was proposed to have the density functional depend on the density gradient without enforcing the correct SO term; such an approximation is called a generalized gradient approximation (GGA),⁴ and GGAs have played a prominent role in the development of DFT, including such well-known and historically important GGAs as BP86,^{5,6} BLYP,^{5,7} PW91,⁸ BPW91,^{5,8} PBE,⁹ OLYP,^{7,10} HCTH407,¹¹ RPBE,¹² revPBE,¹³ and mPWPW.¹⁴ Although the unknown exact functional must be nonlocal¹⁵ (as in so-called hybrid¹⁶ and doubly hybrid¹⁷ functionals), there is considerable interest in GGAs because of their simplicity and low computational cost; a consequence of the former is that essentially every density functional computer program in general use can accommodate GGAs, and for those codes that can accommodate hybrid functionals, the cost for GGAs is often considerably lower, especially for extended systems. Meta-GGA functionals depend

on the local kinetic energy density and provide enhanced performance at only slightly higher cost than GGAs, and they are available in many but not all popular computer programs. Aside from practicality, it is an interesting fundamental question to understand how accurate approximate density functionals can be if they are restricted to be GGAs, that is, to depend only on the density and its gradient (or spin-labeled densities and their gradients for open-shell systems^{18,19}).

Popular GGAs that yield reasonable energetic predictions for chemical problems tend to have a coefficient of the SO term in the gradient expansion of the exchange energy that is about twice as large as the correct value, and we showed that lowering that coefficient (which created a new approximate density functional called SOGGA) makes the energetic predictions much worse, although geometric predictions such as bond lengths and lattice constants are generally improved.²⁰ Only one other GGA correct through second order has received significant attention in the literature; that functional, called PBEsol,²¹ also has good performance for lattice constants and poor accuracy for chemical energetics.

In the present Letter, we re-examine the question of whether one can construct a GGA that satisfies the SO expansion constraint but also leads to reasonably good energetics for molecules. (We do not address the question of extended solids here.) The approach we take is to use a new functional form with

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more flexibility than SOGGA and to optimize it against a broad set of energetic databases, a strategy that has previously been used successfully for meta-GGA²² and hybrid meta-GGA²³ density functionals. We will see that not only can we obtain a GGA that is both correct through SO and reasonably accurate for chemical energetics of normal molecules, but also the resulting density functional, which we call SOGGA11, is actually more accurate on average for the broad range of molecular energetic databases than any previously available GGA, and it is quite accurate for molecular bond lengths as well.

The SOGGA11 Functional section presents the new functional form; the Optimization Strategy section introduces the databases, discusses the optimization strategy, and presents the optimized parameters; and the Performance of the SOGGA11 Functional section has results and discussion, followed by concluding remarks.

SOGGA11 Functional. The new GGA functional form is based on SOGGA²⁰ and other work.^{12,20,24} The main advantages of the new functional form are: (i) flexibility, (ii) ease of imposing key constraints, (iii) easy implementation in quantum chemistry software, and (iv) the possibility of serving as a base for expansion and improvement (e.g., hybrid functionals, range-separated functionals, and meta-GGAs).

Exchange. The functional form for the SOGGA11 exchange is the following extension of the SOGGA form

$$E_x^{\text{SOGGA11}} = \int d^3r \rho \epsilon_x^{\text{LSDA}}(\rho) F_x^{\text{SOGGA11}}(s) \quad (1)$$

where ρ is the electron density, $s = |\nabla\rho|/[2(3\pi^2)^{1/3}\rho^{4/3}]$ is the dimensionless reduced gradient, $\epsilon_x^{\text{LSDA}} = -3/4(3/\pi)^{1/3}\rho^{1/3}$ is the exchange energy density per particle for a uniform electron gas (UEG), and F_x^{SOGGA11} is the SOGGA11 exchange enhancement factor

$$F_x^{\text{SOGGA11}} = \{g_1^x(s) + g_2^x(s)\} \quad (2)$$

$$g_1^x = \sum_{i=0}^m a_i^x \left(1 - \frac{1}{1 - \frac{\mu}{\kappa} s^2} \right)^i \quad (3)$$

$$g_2^x = \sum_{i=0}^m b_i^x (1 - \exp(-\mu s^2/\kappa))^i \quad (4)$$

where μ and κ are parameters determined in the original SOGGA paper by fitting to physical constraints and kept at the same values here.

Correlation. A recent study²⁵ showed that the widely used Stoll ansatz for correlation is inaccurate for a UEG. For SOGGA11, we introduce a new factor inspired by the SOGGA11 exchange

$$E_c^{\text{SOGGA11}} = \int d^3r \rho \epsilon_c^{\text{LSDA}}(\rho, \zeta) F_c^{\text{SOGGA11}}(\rho, \zeta, s) \quad (5)$$

where ϵ_c^{LSDA} is the correlation energy per particle in the UEG limit, $\zeta = (\rho_\uparrow - \rho_\downarrow)/\rho$ is the relative spin polarization, and F_c^{SOGGA11} is the SOGGA11 enhancement factor for correlation

$$F_c^{\text{SOGGA11}} = \{g_1^c(\rho, \zeta, s) + g_2^c(\rho, \zeta, s)\} \quad (6)$$

$$g_1^c = \sum_{i=0}^m a_i^c \left(1 - \frac{1}{1 - \frac{\beta \varphi(\zeta) (3\pi^5)^{1/3} \rho^{1/3} s^2}{4\epsilon_c^{\text{LSDA}}}} \right)^i \quad (7)$$

$$g_2^c = \sum_{i=0}^m b_i^c (1 - \exp(\beta \varphi(\zeta) (3\pi^5)^{1/3} \rho^{1/3} s^2 / 4\epsilon_c^{\text{LSDA}}))^i \quad (8)$$

where $\varphi = [(1 + \zeta)^{2/3} + (1 - \zeta)^{2/3}]/2$ is a spin scaling factor. The Perdew–Wang parametrization²⁶ was used for ϵ_c^{LSDA} .

Fortran routines for the SOGGA11 functional are included in the Supporting Information and also freely available on our webpage within the Minnesota Functional Module.²⁷

Constraints. As in the SOGGA functional, we impose two physical constraints, in particular, the UEG limit and the SO density-gradient expansion. The SOGGA11 functional forms for exchange and correlation have the following SO density-gradient expansions

$$E_x^{\text{SOGGA11}} = \int d^3r \rho \epsilon_x^{\text{LSDA}} \left\{ a_0^x + b_0^x + \frac{\mu}{\kappa} (a_1^x + b_1^x) s^2 + O[s^4] \right\} \quad (9)$$

$$E_c^{\text{SOGGA11}} = \int d^3r \rho \{ \epsilon_c^{\text{LSDA}} (a_0^c + b_0^c) - \beta s^2 (a_1^c + b_1^c) + O[s^4] \} \quad (10)$$

The UEG limit is imposed by

$$a_0^x + b_0^x = 1 \text{ and } a_0^c + b_0^c = 1 \quad (11)$$

and the SO gradient expansion is imposed by setting μ to $\mu^{\text{GE}} = 10/81 = 0.12346$ and β to $\beta_c^{\text{GE}} = 0.066725$, with the following additional conditions

$$a_1^x + b_1^x = \kappa \text{ and } a_1^c + b_1^c = -1 \quad (12)$$

Databases. Many databases have been compiled and used in our group for the optimization of new DFT functionals. In the compilation of the present training set, particular emphasis has been placed on main-group and transition metal thermochemistry, kinetics, π interactions, and noncovalent interactions. The current training set is composed of 322 data, divided into 15 databases that we briefly introduce here. The total set of 322 data is called BC322 (broad chemistry database with 322 elements). A more detailed presentation of each of the databases comprising BC322 is collected in the Supporting Information and the references.^{22,23,28–58}

Eleven databases from previous work have been collected in the training set, namely: MGAE109/05²⁸ for main group atomization energies, IP13/03^{28,39–41} for ionization potentials, EA13/03^{28,39–41} for electron affinities, PA8⁴² for proton affinities, ABDE4/05^{22,28,45} for alkyl bond dissociation reaction energies, HC7/11 for hydrocarbons, HTBH38/08^{28,48,49} and NHTBH38/08^{28,48,49} for hydrogen transfers and non-hydrogen transfers barrier heights, π TC13^{22,40,42} for interactions in π systems, NCCE31/05^{39,50} for noncovalent complexes, and AE17^{23,51} for atomic energies. Two new databases are used here: the ISOL6/11 database with six isomerization energies of large organic molecules (updated from previous work of Grimme³³) and ABDEL8, a set of alkyl bond dissociation energies that is more extensive than ABDE4/05 and that contains larger molecules. The ABDEL8 database includes eight R–X bond dissociation energies of molecules

with R = ethyl and *tert*-butyl and X = H, CH₃, OCH₃, OH. We believe that it is important to examine these bond energies, especially for the larger alkyl groups like *tert*-butyl, because good performance for atomization energies of small molecules does not guarantee good performance for such quantities. Finally, two previous databases^{53,54} have been restructured into a new database, SRMBE12, of 12 single-reference metal bond dissociation energies and another new database, MRMBE5, of multireference metal bond energies; both of these databases contain both metal–metal and metal–ligand bond energies. We note that we found that performance on SRMBE12 tends to correlate with performance on MGAE109/05, but this is not true for MRMBE5.

In addition to deciding which data to include, it is important to decide which data not to include. For example, there are some data that no GGA seems to be able to predict well. It seems evident that the inability to predict the energies of these systems is more a drawback of the restrictions of the GGA itself than of individual GGAs; we therefore believe that including such data in a GGA parametrization would simply build in unphysical cancellations of errors to reduce large errors to moderate ones without significantly improving performance for the many kinds of problems for which GGAs are useful. Examples of such data are the atomization energy of ozone, the energy of the reaction $\text{P}_4\text{O}_{10} \rightarrow \text{P}_4 + 5\text{O}_2$, and other data included in our previous DC10 database.²³

Geometries, Basis Set, Relativistic Effects, Software. The MG3S basis⁴¹ was used for MGAE109/05, IP13/03, EA13/03, PA8/06, ABDE4/05, ABDEL8, and πTC13 , the 6-311+G(2df,2p) basis⁴⁴ was used for HC7/11, and the MG3SXP basis⁵⁹ was used for ISOL6/11. All energetic databases, except SRMBE12 and MRMBE5, are calculated with single-point energy calculations at geometries reported in the Supporting Information. Geometries for the molecules in SRMBE12 and MRMBE5 are optimized consistently with each level of theory, using the def2-TZVP basis^{60,61} set. The final SOGGA11-optimized geometries are all within 0.01 Å of the experimental geometry.

Scalar relativistic effects were not included in main-group compounds and 3d transition metals. Scalar relativistic effects for the 4d transition metals in the metals databases are taken into account by using the relativistic effective core potential of the def2-TZVP basis set. The vector relativistic effect is included by adding spin–orbit coupling to atoms and open-shell molecules for which it is nonzero, as previously described.²²

All calculations in this Article were performed with a locally modified version of the *Gaussian 09* program⁶² using the ultrafine (99,590) Lebedev grid and allowing breaking of the symmetry of the wave function to converge to the broken symmetry solution (through the `Stable=Opt Gaussian` keyword).

Optimization. The optimization procedure consists of minimizing a training function, F , defined by

$$\begin{aligned} F = & w_1 R_p(\text{MGAE109/05}) + w_2 R(\text{ISOL6/11}) \\ & + w_3 R(\text{IP13/03}) + w_4 R(\text{EA13/03}) \\ & + w_5 R(\text{PA8/06}) + w_6 R(\text{ABDE4/05}) \\ & + w_7 R(\text{ABDEL8}) + w_8 R(\text{HC7/11}) \\ & + w_9 R(\pi\text{TC13}) + w_{10} R(\text{HTBH38/08}) \\ & + w_{11} R(\text{NHTBH38/08}) \\ & + w_{12} R(\text{NCCE31/05}) + w_{13} R(\text{AE17}) \\ & + w_{14} R(\text{SRMBE12}) + w_{15} R(\text{MRMBE5}) \end{aligned} \quad (13)$$

where w_n is a weight and $R(\text{D})$ and $R_p(\text{D})$ are, respectively, the root-mean-squared error and the root-mean-squared error per bond of database D.

Table 1. Optimized Parameters for the Exchange and the Correlation of SOGGA11

	exchange	correlation
a_0	5.00000×10^{-1}	5.00000×10^{-1}
a_1	−2.95535	−4.62334
a_2	1.57974×10^1	8.00410
a_3	$−9.11804 \times 10^1$	$−1.30226 \times 10^2$
a_4	9.62030×10^1	3.82685×10^1
a_5	1.86830×10^{-1}	6.95599×10^1
b_0	5.00000×10^{-1}	5.00000×10^{-1}
b_1	3.50743	3.62334
b_2	$−1.29523 \times 10^1$	9.36393
b_3	4.97870×10^1	3.45114×10^1
b_4	$−3.32545 \times 10^1$	$−1.85684 \times 10^1$
b_5	$−1.11396 \times 10^1$	$−1.65195 \times 10^{-1}$

By changing the weights, we can influence the behavior of the resulting functional. This could be used to create specialized functionals for particular chemical properties (e.g., for chemical kinetics, by giving more emphasis to w_{10} and w_{11} , or for main-group thermochemistry, by increasing the values of w_1 to w_9 , etc.) or to create a functional for general use, by adjusting the weights to achieve broad performance over all databases. We followed the latter strategy.

We studied the convergence of the results as a function of the number of terms in the expansion series (eqs 3, 4, 7, and 8) as well as the behavior of the global functional as a function of the weights by using post-SCF calculations. We found that good convergence is achieved at $m = 4$ or 5 for both the exchange and the correlation, and we elected to stop at $m = 5$ leading to a total of 24 parameters. As shown in the previous section, the first four parameters are determined by imposing the UEG (eq 11), whereas two of the coefficients of the first-order terms are determined by imposing the SO expansion (eq 12). This brings down the number of empirically fitted parameters to 18. After this first analysis at the post-SCF level, the 18 free coefficients of SOGGA11 are optimized self-consistently (for fixed weights). The final values are in Table 1; the weights used in the training function (eq 13) for the optimization that yielded these coefficients are reported in the first column of Table 2. The weights are used only in eq 13; they are not involved in the calculations of the MUEs reported in the Table or in our further considerations regarding the performance of the functionals.

Performance of the SOGGA11 Functional. We compare the performance of the newly created SOGGA11 functional with those of a large number of common GGAs. In addition to the GGAs mentioned in the Introduction, we compare to two meta-GGAs, namely, TPSS and M06-L. SOGGA11, PBEsol, SOGGA, and TPSS are the only functionals in Table 2 that are correct to SO in the density-gradient expansion. Results for the mean unsigned error (MUE) of these functionals on the databases that comprise the training set are collected in Table 2. Results on subsets of the databases that can be used to evaluate the performance of each density functional for a particular class of compounds or properties are collected in the Supporting Information along with signed errors for all calculated data in this Letter.

The overall performance of each functional is evaluated by using the MUE over the total set of 322 data in the training set

Table 2. Mean Unsigned Errors (MUEs) in kilocalories per mole for the Energetic Databases

database	w_n^a	GGAs													meta-GGAs	
		SOGGA11	OLYP	BPW91	RPBE	HCTH407	mPWPW	revPBE	BLYP	PW91	BP86	PBE	PBEsol	SOGGA	M06-L	TPSS
MGAE109/05	50	1.56	0.88	1.36	1.92	1.07	2.00	1.62	1.54	3.16	4.19	2.99	7.78	7.65	0.85	1.04
ISOL6/11	25	1.73	3.44	2.38	2.99	3.02	2.16	2.82	3.73	1.92	2.71	1.98	1.55	1.89	2.76	3.66
IP13/03	13	4.74	2.60	3.74	3.12	5.46	4.19	3.07	4.71	4.54	6.47	3.62	2.66	2.48	3.08	3.09
EA13/03	3	5.23	3.60	2.26	2.37	3.70	2.30	2.39	2.76	2.60	4.97	2.27	2.16	2.70	3.83	2.35
PA8/06	6	2.11	2.40	1.88	1.98	2.84	1.52	2.00	1.58	1.30	1.56	1.34	2.10	2.33	1.88	2.66
ABDE4/05	10	5.00	10.28	8.37	11.21	9.05	6.31	10.59	10.60	3.82	7.09	4.09	4.03	5.09	5.54	9.56
ABDEL8	10	7.89	12.12	10.85	13.49	11.61	9.01	12.94	12.18	6.80	9.88	7.16	3.18	3.87	8.85	10.93
HC7/11	2	6.26	17.01	10.77	14.96	14.97	8.08	13.65	27.39	4.55	10.70	3.97	13.31	17.88	3.35	10.48
π TC13	7	7.61	9.99	8.85	8.95	9.85	8.27	8.90	7.80	7.62	5.97	7.40	5.50	5.20	8.16	9.75
HTBH38/08	30	6.57	5.63	7.38	6.43	5.48	8.43	6.58	7.52	9.60	9.70	9.31	12.69	12.88	4.15	7.71
NHTBH38/08	10	4.32	5.25	7.26	6.82	6.29	8.03	6.82	8.85	8.80	10.37	8.42	9.86	9.68	3.81	8.91
NCCE31/05	20	1.28	2.39	1.69	1.46	1.14	1.26	1.59	1.55	1.37	2.12	1.24	1.79	1.84	0.58	1.17
AE17	2	6.99	6.89	8.35	7.99	12.86	9.62	15.51	8.67	7.78	17.05	54.44	253.24	290.38	3.86	13.61
SRMBE12	3	4.32	9.58	3.91	3.30	5.57	3.50	3.24	7.10	8.24	5.33	3.87	6.04	6.04	3.41	3.16
MRMBE5	2	7.12	4.83	5.32	4.68	6.38	5.85	5.19	4.99	6.48	6.90	6.74	9.41	9.41	6.95	5.22
BC305		3.59	4.03	4.09	4.26	4.00	4.34	4.13	4.96	5.02	5.97	4.64	7.13	7.24	2.73	4.21
BC322		3.77	4.19	4.32	4.46	4.47	4.62	4.74	5.16	5.17	6.56	7.27	20.13	22.19	2.79	4.71

^aData in this column are the relative weights (un-normalized) of each database, w_n , in the SOGGA11 training function (eq 13); these weights are not used for computing the mean errors reported in the Table.

and is reported in Table 2 in the BC322 line. The inability to treat absolute atomic energies is a known issue of many GGA functionals. For this reason, we recalculated the global MUE without the atomic energies of the AE17 database and reported it in Table 2 as BC305. According to either of these overall MUEs, SOGGA11 emerges as the best GGA functional overall, at least for all GGAs tested. (It would be interesting to test more functionals,⁶³ such as the one of Vela et al.,⁶⁴ in future work.)

We found in a previous work²⁰ that functionals that restore the SO expansion in the density gradient provide, in general, very good geometries. For this reason, we also tested the new SOGGA11 functional for its performances on the MGBL19²² database of 19 main-group bond lengths. This database can be divided into MGHBL9 with nine hydrogenic bond lengths (HBLs) and MGNHBL10 with 10 nonhydrogenic bond lengths (NHBLs). This test is in Table 3, and it shows that the SOGGA11 functional, although optimized entirely on energetic data, provides better performance for bond lengths than all GGAs tested except HCTH407, which is slightly better.

The SOGGA11 exchange enhancement factor F_x as a function of s is shown in Figure 1, which shows that the SOGGA11 enhancement factor is more similar to the M06-L factor than to the other GGA functionals. Figure 2 shows the behavior of enhancement factors as functions of s^2 in the small- s region; this Figure clearly illustrates the separation into functionals with the correct coefficient of s^2 , functionals with a coefficient about twice as large as the correct value, and the HCTH407 functional, which is not even correct at $s = 0$. This is a good place to stress that the SOGGA11 exchange functional is designed to be used only in conjunction with the SOGGA11 correlation functional, and the correlation form is also responsible for the good performance of the functional.

In this work, we collected and in some cases revised 15 databases for chemical energetics, and we used them to determine the coefficients of a new exchange–correlation functional,

Table 3. Mean Unsigned Errors (MUEs) for Hydrogenic and Nonhydrogenic Bond Distances (angstroms) in the MGBL19 Database

	MGHBL9	MGNHBL10	MGBL19
GGAs			
HCTH407	0.003	0.005	0.004
SOGGA11	0.003	0.006	0.005
OLYP	0.007	0.007	0.007
mPWPW	0.009	0.008	0.008
PW91	0.010	0.007	0.008
BPW91	0.010	0.008	0.009
PBE	0.011	0.008	0.009
PBEsol	0.014	0.006	0.010
SOGGA	0.015	0.006	0.010
BP86	0.012	0.009	0.010
revPBE	0.012	0.012	0.012
RPBE	0.011	0.013	0.012
BLYP	0.011	0.015	0.013
meta-GGAs			
M06-L	0.002	0.004	0.003
TPSS	0.007	0.007	0.007

called SOGGA11, that is a GGA correct to the SO in the density-gradient expansion. The SOGGA11 functional is the first functional correct to SO that not only provides reliable geometries but also has relatively small errors for a diverse set of energetic data; in fact, it predicts more accurate molecular energetics, on average, than any previous GGA that we tested, even those that sacrifice satisfaction of the SO constraint to improve performance for energetics. SOGGA11 also has excellent performance

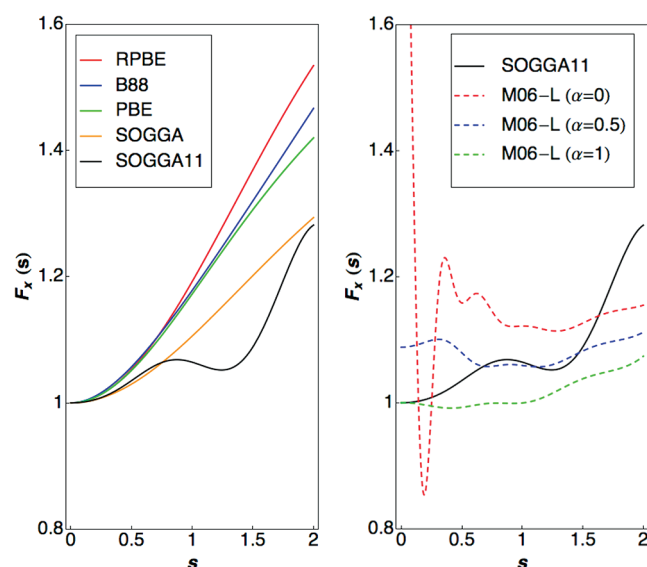


Figure 1. Analysis of the exchange enhancement factor of different functionals as a function of the reduced gradient s , in the significant region for chemical interactions $0 \leq s \leq 2$. The solid black curve is SOGGA11; solid-colored curves are other GGAs; and dashed colored curves are M06-L for various values of the parameter α , where α , as defined in the Supporting Information of ref 63 is a unitless variable equal to the deviation of the kinetic energy density from the von Weizsäcker value, as scaled by the LSDA value. The PW91 functional is not shown but is very similar (lower but by <1%) to the PBE one over the range plotted.

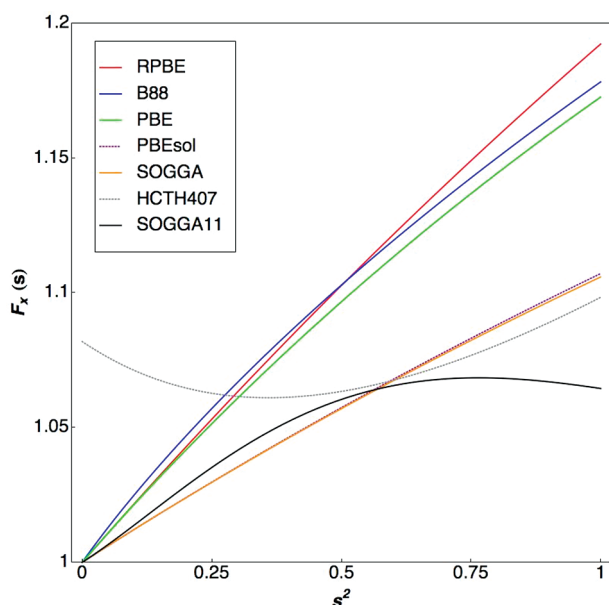


Figure 2. Exchange enhancement factor of different functionals as a function of s^2 in the small- s region. Notice that the SOGGA and PBEsol curves are very similar over the range plotted.

for predicting molecular bond lengths. The dependence on reduced density gradient of the exchange enhancement factor of the new functional is more similar to that of the M06-L meta-GGA than to that of previous GGAs.

■ ASSOCIATED CONTENT

S Supporting Information. Details of databases, results, and optimized geometries; FORTRAN program. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: truhlar@umn.edu.

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