Communication: A global hybrid generalized gradient approximation to the exchange-correlation functional that satisfies the second-order density-gradient constraint and has broad applicability in chemistry

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We extend our recent SOGGA11 approximation to the exchange-correlation functional to include a percentage of Hartree-Fock exchange. The new functional, called SOGGA11-X, has better overall performance for a broad chemical database than any previously available global hybrid generalized gradient approximation, and in addition it satisfies an extra physical constraint in that it is correct to second order in the density-gradient. © *2011 American Institute of Physics*. [doi:10.1063/1.3663871]

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 development of improved approximations to the exchange-correlation functional has been a crucial ingredient in the success of DFT, and the introduction of the first hybrid functional[3] was a key ingredient in the establishment of DFT as a preferred tool for chemical calculations.

The approximate functional proposed in the original Kohn-Sham paper[4] depends only on the electron density. The leading correction for nonuniform density, as required to treat real systems, enters at second order in the density gradient, but truncation of the density expansion of the exchange functional at second order does not yield a good global approximation to the exchange hole, so it was proposed to have the functional depend locally on the density gradient without enforcing the correct second order term; such a local approximation is called a generalized gradient approximation (GGA),[5] and GGAs have played a prominent role in the development of DFT, although the unknown exact functional must be nonlocal.[6] Popular GGAs that yield reasonable energetic predictions for chemical problems usually have a coefficient of the second order term in the gradient expansion of the exchange energy that is about twice as large as the correct value. However, by improving the flexibility of the functional form and by designing a careful optimization procedure, we were recently able to provide a GGA functional, called SOGGA11,[7] that has the correct coefficient of the second order term and provides good across-the-board performance for chemical systems.

Hybrid GGAs replace a percentage of the local exchange by Hartree-Fock (HF) exchange, and in global hybrids this percentage is a constant, independent of density, density gradient, interelectronic distance, or position in space. The first broadly successful hybrid functional, B3PW91,[8] and its close cousin, B3LYP,[9] were global hybrid GGAs. More accurate global hybrid GGAs, such as B98 (Ref. 10) and B97-3,[11] both based on an earlier GGA functional form introduced by Becke,[12] have also been introduced, as has PBE0,[13] with a simpler functional form.

More advanced and accurate functionals have been developed throughout the years, such as meta-GGAs,[14] hybrid meta-GGAs,[15] doubly hybrid functionals,[16] and range-separated hybrid functionals,[17] but GGAs and global hybrid GGAs still remain the most used functionals for chemical applications, probably because their simplicity has contributed to their wide availability in popular quantum chemistry computer programs; in fact, the B3LYP global hybrid GGA functional is still the most popular functional in most areas of quantum chemistry, despite its known shortcomings. In part, this is true because DFT is now widely used by nonspecialists, and the early successes of B3LYP gave it a good reputation and made it hard to displace even with better performing global hybrid GGAs, such as B97-3,[11] mPW1PW,[18] and MPW1K.[19] Given the simplicity and popularity of global hybrid GGAs, the question arises of how well a global hybrid can do. From the point of view of main-group heats of formation, this was largely answered many years ago with the B98 functional.[10] Here, we broaden the inquiry to include other properties such as barrier heights, noncovalent interaction energies, and bond energies. For this broader subset, the best global hybrid GGA (prior to the work reported here) is B97-3. In this communication, we use the same conceptual framework that drove the development of the SOGGA11 GGA to develop a new global hybrid GGA, called SOGGA11-X, and we optimize it for across-the-board performance. The new functional is also distinguished by being the first global hybrid GGA correct to second order for both exchange and correlation.

The optimization depends on two factors: (i) the functional form, that must be physically appropriate and flexible enough to catch the bulk of the possible systematic improvements, but not too flexible, in order to avoid over-fitting, and (ii) the databases used in the process, that must include a large number of data for different properties, avoiding, however,

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data that are beyond the predictive ability of the chosen functional form (in this case a global hybrid GGA).

Databases: As in the database used for testing SOGGA11, particular emphasis has been placed on main-group and transition metal thermochemistry, kinetics, and noncovalent interactions. The database used here is composed of 317 data, divided into 14 subdatabases. The total set of 317 data is called BC317 (broad chemistry database with 317 elements).

The subdatabase containing main group atomization energies[20] is updated here to MGAE109/11, by replacing 41 data based on experimental results by 41 new reference data from Karton *et al.*,[21] obtained with W4,[22] W4.2,[22] W4.3,[22] and W4.4 (Ref. [23]) calculations.[24] The other subdatabases used in BC317 are carried over from previous work[7] and are: ISOL6/11 for isomerization energies of large organic molecules, IP13/03 (Refs. [15], [20], [25], and [26]) for ionization potentials, EA13/03 (Refs. [15], [20], [25], and [26]) for electron affinities, PA8 (Ref. [27]) for proton affinities, ABDE4/05 (Refs. [20], [28], and [29]), and ABDEL8 for alkyl bond dissociation energies, HC7/11 containing seven difficult cases involving medium-range correlation energies in hydrocarbons,[30] HTBH38/08 (Refs. [20] and [31]) and NHTBH38/08 (Refs. [20] and [31]) for barrier heights of hydrogen transfers and non-hydrogen transfer reactions, πTC13 (Refs. [15], [27], and [28]) for thermochemistry in π systems, NCCE31/05 (Refs. [25] and [32]) for diverse kinds of noncovalent complexation energies, AE17 (Refs. [17] and [33]) for atomic energies, and SRMBE12,[7] containing twelve single-reference metal bond dissociation energies.

Geometries, basis set, relativistic effects, software: All energetic results are calculated with single-point energy calculations using appropriate basis sets[26,34,35] and geometries reported in the references already given. Relativistic effects are taken into account as described previously.[7,28] All SOGGA11-X calculations in this communication were performed with a locally modified version of the GAUSSIAN09 program[36] and allowing the wave function to break symmetry in order to converge to a stable solution (through the STABLE = OPT keyword of GAUSSIAN09). The ultrafine (99,590) Lebedev grid was used for integrating the energy density; however, as with other global hybrid GGAs, a fine (75,302) grid is generally sufficient to provide good convergence and numerical stability.

Functional form: We use

$$E_{xc}^{\text{SOGGA11-X}} = \left(\frac{X}{100}\right)E_x^{\text{HF}} + \left(1 - \frac{X}{100}\right)E_x^{\text{SOGGA11}} + E_c^{\text{SOGGA11}}, \tag{1}$$

where E_x^{HF} is the Hartree-Fock exchange energy calculated from the occupied Kohn-Sham spin-orbitals, and the other terms are density-dependent and take the same form (Eqs. (1)–(10) in Ref. [7]) as used in SOGGA11 with newly optimized coefficients a_i and b_i for the exchange and correlation. FORTRAN routines for the density-dependent terms are given in the supplementary material and on our webpage within the Minnesota Functional Module.[37]

Constraints: As in SOGGA (Ref. [38]) and SOGGA11,[7] we impose two physical constraints, in particular, the uniform electron gas (UEG) limit and the second-order density-gradient expansion (SO). The HF exchange energy expression yields the exact density functional exchange energy when applied with the pair density obtained from a Slater determinant formed from the exact Kohn-Sham orbitals.[39] Therefore, the Hartree-Fock energy expression is formally exact and has the correct density gradient expansion by definition.[40] To enforce the second-order constraint on the hybrid exchange functional, we need merely to constrain the GGA part. The UEG limit is imposed by

$$a_0^x + b_0^x = 1, \qquad a_0^c + b_0^c = 1, \tag{2}$$

and the second order gradient expansion is imposed by setting μ to $\mu^{\text{GE}} = \frac{10}{81} = 0.12346$ and β to $\beta_c^{\text{GE}} = 0.066725$, with the following conditions on the coefficients:

$$a_1^x + b_1^x = \kappa = \frac{1.9555}{2^{1/3}} - 1 \cong 0.552, \qquad a_1^c + b_1^c = -1. \tag{3}$$

We also enforce a positivity condition on the entire enhancement factor for the exchange

$$F_x^{\text{SOGGA11}}(s) \geq 0 \ \forall s \in (0, \infty). \tag{4}$$

Optimization: The optimization procedure consists of minimizing an unfitness function, F, defined by

$$\begin{aligned}
F = \ &w_1 R_p(\text{MGAE109/05}) + w_2 R(\text{ISOL6/11}) \\
&+ w_3 R(\text{IP13/03}) + w_4 R(\text{EA13/03}) + w_5 R(\text{PA8/06}) \\
&+ w_6 R(\text{ABDE4/05}) + w_7 R(\text{ABDEL8}) + w_8 R(\text{HC7/11}) \\
&+ w_9 R(\text{pTC13}) + w_{10} R(\text{HTBH38/08}) \\
&+ w_{11} R(\text{NHTBH38/08}) + w_{12} R(\text{NCCE31/05}) \\
&+ w_{13} R(\text{AE17}) + w_{14} R(\text{SRMBE12}), \tag{5}
\end{aligned}$$

where w_n is a weight, and $R(\mathscr{D})$ and $R_p(\mathscr{D})$ are, respectively, the root-mean-squared error and the root-mean-squared error per bond of database $\mathscr{D}$. The weights that we used are those that minimize the value of the unfitness function and at the same time, provide better performance than SOGGA11 and B97-3 for at least 13 of the 14 subdatabases in BC317. Weights are not used in the calculation of the final performance of the functional or the functionals to which it is compared; the weights are just a part of the optimization process used to get good across-the-board performance for the various subdatabases.

We use the same number of polynomial terms as in SOGGA11, so we cut the expansion series at $m = 5$ for both the exchange and the correlation, leading to 24 coefficients. The numbers that are freely adjustable is six less because of the constraints explained above. We also optimize the percentage X of HF exchange, leading to a total of 19 empirically fitted parameters. The final values are in Table I; the weights used in Eq. (5) for the optimization that yielded these coefficients are reported in Table II.

As an illustration of the numerical stability of the fitting procedure, we plot the SOGGA11-X exchange enhancement factor, F_x, as a function of the finite reduced gradient u

TABLE I. Optimized parameters for the exchange and the correlation of SOGGA11-X.

	Exchange	Correlation
a_0	5.00000×10^{-1}	5.00000×10^{-1}
a_1	5.37406×10^{0}	7.82439×10^{1}
a_2	-5.94160×10^{0}	2.57211×10^{1}
a_3	1.27962×10^{1}	-1.38830×10^{1}
a_4	-1.88521×10^{1}	-9.87375×10^{0}
a_5	8.78551×10^{0}	-1.41357×10^{1}
b_0	5.00000×10^{-1}	5.00000×10^{-1}
b_1	-4.82197×10^{0}	-7.92439×10^{1}
b_2	5.40713×10^{0}	1.63725×10^{1}
b_3	-4.10014×10^{0}	2.08129×10^{0}
b_4	-6.27393×10^{0}	7.50769×10^{0}
b_5	6.62678×10^{0}	-1.01861×10^{1}
X	40.15	

FIG. 1. Analysis of the exchange enhancement factor of five functionals as functions of the finite reduced gradient u. The black curve is SOGGA11-X; other curves are for GGA exchange functionals.

(Ref. 41) (equal to $s^2/(1 + s^2)$, where s is the usual[38] dimensionless reduced gradient) in Fig. 1. The SOGGA11-X enhancement factor resembles those of SOGGA and SOGGA11 at small u but then starts to separate from them. This is a consequence of the SOGGA11-X enhancement factor being optimized for use with nonlocal HF exchange, while all others are not. Moreover, the SOGGA11-X exchange is optimized in conjunction with its correlation, and we caution readers that using the exchange or correlation functional independent of the partner with which it was optimized is not recommended.

Overall, the SOGGA11-X curve is better behaved than that of the SOGGA11, since it is smoother, positive, and without large oscillations over the entire range of u.

Performance: Table II compares the mean unsigned error (MUE) on the subdatabases of BC317 for various GGAs (PBE (Ref. 42) and SOGGA11 (Ref. 7)), global hybrid

TABLE II. Mean unsigned errors in kcal/mol for the subdatabases and the whole BC317 database.

		GGA		Global Hybrid GGA									Hybrid meta-GGA	
Database	w_n[a]	PBE	SOGGA11	PBE0[b]	B1LYP	B3LYP	mPW1PW	O3LYP	B3PW91	B98[c]	B97-3	SOGGA11-X	M06	M11
No. of parameters[d]		0	18	1	1	3	1	3	3	16	19	19	38	38
X		0	0	25	25	20	25	11.61	20	21.98	26.93	40.15	27	42.8-100
MGAE109/11[e]	55	7.75	1.64	0.95	2.70	0.96	0.99	0.80	0.71	0.69	0.64	0.71	0.60	0.51
ISOL6/11	25	1.55	1.73	1.38	2.70	2.61	1.44	2.82	1.52	1.93	2.07	1.85	1.27	1.10
IP13/03	13	2.66	4.74	3.24	3.75	4.76	3.76	2.47	4.30	3.23	3.54	3.20	3.28	3.64
EA13/03	3	2.16	5.23	2.79	3.69	2.33	2.68	2.97	2.13	1.90	2.13	1.55	1.85	0.89
PA8/06	5	2.10	2.11	1.19	1.06	1.02	1.77	2.36	1.89	1.53	2.54	1.85	1.84	1.03
ABDE4/05	12	4.03	5.00	5.14	10.57	8.73	6.94	9.13	7.43	4.99	4.74	4.68	2.84	2.45
ABDEL8	10	3.18	7.89	8.11	12.16	10.40	9.59	10.93	9.79	7.71	7.70	5.12	4.72	3.48
πTC13	10	4.84	7.61	6.05	5.98	6.06	6.69	7.90	6.89	7.01	7.10	5.78	4.08	2.12
HTBH38/08	35	12.69	6.57	4.22	3.19	4.23	3.55	4.06	4.02	4.16	2.28	1.79	1.98	1.30
NHTBH38/08	15	9.86	4.32	3.43	3.63	4.55	5.71	3.64	3.62	3.31	1.38	1.16	2.33	1.28
NCCE31/05	25	1.79	1.28	0.69	0.97	0.96	0.73	1.93	1.15	0.70	0.98	0.63	0.41	0.26
AE17	10	253.24	6.99	45.25	6.87	13.62	7.97	3.39	10.34	9.25	9.24	5.26	6.85	5.15
HC7/11	2	13.31	6.26	9.40	17.64	16.80	6.70	12.52	4.35	8.46	7.58	7.27	2.78	3.74
SRMBE12	3	6.04	9.09	2.6	6.19	2.88	2.38	3.38	2.73	2.64	3.59	3.28	2.77	4.55
BC317		20.26	3.92	4.86	3.90	3.67	3.13	3.02	2.99	2.81	2.43	1.93	1.90[f]	1.48[f]

[a]These weights are used during optimization of SOGGA11-X but not for computing the mean errors reported in the table.
[b]Also called PBE1PBE and PBEh.
[c]Using formula (2c) in Ref. 10.
[d]Number of parameters does not include inherited parameters (such as the LYP parameters in B3LYP or the UEG correlation fitting parameters in most of the functionals) nor does it count empirical choices of which constraints to employ.
[e]Errors for the MGAE109/11 subdatabase are reported as mean unsigned error per bond.
[f]The MUEs for other Minnesota functionals on the BC317 database are: M06-2X, 1.41; M08-HX, 1.51; M05-2X, 1.66; M08-SO, 1.83; M06-HF, 2.03; M05, 2.36; M06-L, 2.66.

GGAs (B1LYP,[43] PBE0,[13] B3LYP,[8,9] mPW1PW,[18] O3LYP,[44] B3PW91,[8,45] B98,[10] and B97-3[11]), and meta-GGAs (M06 (Ref. [46]) and M11 (Ref. [47])). The overall performance of each functional is evaluated by using the MUE over the total set of 317 data and is reported in the last row of Table II. According to this row, SOGGA11-X emerges as the best global hybrid GGA functional, at least of all the ones tested in this work (but the ones tested are a combination of the most popular ones and the ones we anticipated to perform best so we are confident that this is an adequate comparison). More important than the overall MUE is that for all databases SOGGA11-X is either the top performer or comes very close to it. It is especially encouraging that it is the top performer among global hybrid GGA functionals for alkyl-bond dissociation energies (both ABDE4/05 and ABDEL8), barrier heights (both HTBH38/08 and NHTBH38/08), and noncovalent interactions. As expected, SOGGA11-X is not quite as good as the Minnesota hybrid meta-GGA functionals, which have one more ingredient (kinetic energy density) than a GGA.

Conclusion: In this work, we present a new global hybrid GGA functional called SOGGA11-X that is correct to the second order in the density-gradient expansion and that provides the best across-the-board performance among global hybrid GGAs for a diverse set of energetic databases. Because SOGGA11-X is intentionally limited to the popular global-hybrid GGA class of functional, it cannot perform as well as the best available hybrid meta-GGA functionals, but it does illustrate what can be achieved by a "best in class" global hybrid GGA, and it can be useful when software, algorithmic considerations, or grid requirements demand a simpler functional form. On the BC317 broad chemistry database, SOGGA11-X is on an average 15% more accurate than the previously most successful global hybrid GGA (B97–3) and 44% better than the popular B3LYP global hybrid GGA.

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