



Improving the Accuracy of Hybrid Meta-GGA Density Functionals by Range Separation

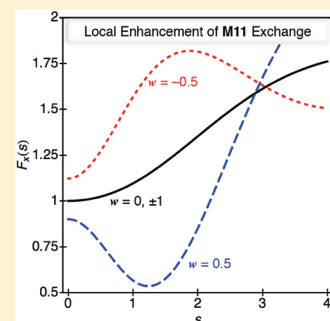
Roberto Peverati and Donald G. Truhlar*

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

S Supporting Information

ABSTRACT: The Minnesota family of exchange–correlation functionals, which consists of meta generalized gradient approximations (meta-GGAs) and global-hybrid meta-GGAs, has been successful for density functional calculations of molecular structure, properties, and thermochemistry, kinetics, noncovalent interactions, and spectroscopy. Here, we generalize the functional form by using range-separated hybrid meta-GGA exchange. We optimize a functional, called M11, with the new form against a broad database of energetic chemical properties and compare its performance to that of several other functionals, including previous Minnesota functionals. We require the percentage of Hartree–Fock exchange to be 100 at large interelectronic distance, and we find an optimum percentage of 42.8 at short range. M11 has good across-the-board performance and the smallest mean unsigned error over the whole test set of 332 data; it has especially good performance for main-group atomization energies, proton affinities, electron affinities, alkyl bond dissociation energies, barrier heights, noncovalent interaction energies, and charge-transfer electronic excitation.

SECTION: Molecular Structure, Quantum Chemistry, General Theory



The development of improved approximations to the exchange–correlation functionals has been a crucial ingredient in the success of density functional theory (DFT).^{1,2} In local density functionals, like PBE and M06-L, the exchange–correlation energy density at a point in space depends on, at most, the spin-labeled densities (ρ_σ), their reduced gradients (s_σ), and the spin-labeled kinetic energy densities (τ_σ) at that point. Popular local functionals include generalized gradient approximations (GGAs), which depend on ρ_σ and s_σ , and meta-GGAs, which also depend on τ_σ .

The unknown exact functional, however, must be nonlocal³ because the exchange–correlation energy density at a point in space depends on functions over the whole range of space. Approximate nonlocal functionals usually involve Hartree–Fock (HF) exchange, which involves the occupied Kohn–Sham⁴ orbitals, which are themselves functionals of the density. The original hybrid functionals,⁵ sometimes called global hybrids, replace a percentage X of local exchange by HF exchange, where X is a global constant. (In doubly hybrid functionals,⁶ one also replaces a fraction of the local correlation by correlation described in terms of orbitals that are unoccupied in the dominant configuration). Another approach to introducing nonlocality was first proposed by Savin⁷ and has been applied with promising results to many functionals at the GGA level. In this approach, the interelectronic Coulomb operator is partitioned into long-range and short-range parts, and different treatments are employed for the long-range and short-range operators; in particular, X becomes a function of interelectronic separation. Some recent functionals of this type, often called range-separated hybrid GGAs (RSH-GGAs), are HSE03,⁸ CAM-B3LYP,⁹

RSHXPBE,¹⁰ LC- ω PBE,¹¹ LCgau-BOP,¹² PBE/CCSD,¹³ and ω B97X.¹⁴

The application of range separation to meta-GGA hybrids is a natural extension of the concepts introduced above, and we propose here a new functional, called M11, that puts this approach into practice. The new functional is balanced to provide accurate performance for a broad range of chemical properties. The general formulation is

$$E_{xc}^{M11} = \left(\frac{X}{100}\right)E_x^{HF} + \left(1 - \frac{X}{100}\right)(E_x^{LR-HF} + E_x^{SR-M11}) + E_c^{M11} \quad (1)$$

where E_x^{HF} is the full-range nonlocal Hartree–Fock exchange, and both the local exchange E_x^{SR-M11} and the local correlation E_c^{M11} depend on ρ_σ , s_σ , and τ_σ . The local exchange is restricted to the short range (SR-M11) and combined with long-range non-local Hartree–Fock (LR-HF) exchange. We will explain the functional for a closed-shell system, where we can dispense with the spin labels (the σ subscripts), but the extension to open shells is standard.

Exchange. The most common splitting operator for the electron–electron interaction is based on the standard error

Received: August 26, 2011

Accepted: October 18, 2011

Published: October 18, 2011

function

$$\frac{1}{r_{12}} = \frac{\text{erf}(\omega r_{12})}{r_{12}} + \frac{\text{erfc}(\omega r_{12})}{r_{12}} \quad (2)$$

where ω is the range parameter. The short-range part of the M11 functional, $E_{\text{x}}^{\text{SR-M11}}$, is calculated with a modification of the original M08¹⁵ exchange as

$$E_{\text{x}}^{\text{SR-M11}} = \int \text{d}\mathbf{r} \, \varepsilon_{\text{x}}^{\text{SR-LSDA}}(\rho) \{f_1(w)F_{\text{x}}^{\text{PBE}}(s) + f_2(w)F_{\text{x}}^{\text{RPBE}}(s)\} \quad (3)$$

where

$$s = \frac{|\nabla\rho|}{2(3\pi^2)^{1/3}\rho^{4/3}} \quad (4)$$

and where we introduce the range separation in the local spin density approximation (LSDA) term by using the formulation proposed by Chai and Head-Gordon,¹⁴ with

$$\varepsilon_{\text{x}}^{\text{SR-LSDA}} = -\frac{3}{2}\left(\frac{3}{4\pi}\right)^{1/3}\rho^{4/3}G(\alpha) \quad (5)$$

where

$$\alpha = \frac{\omega}{2(6\pi^2\rho)^{1/3}} \quad (6)$$

is the dimensionless parameter controlling the attenuation and

$$G = 1 - \frac{8}{3}\alpha \left[\sqrt{\pi} \text{erf}\left(\frac{1}{2\alpha}\right) - 3\alpha + 4\alpha^3 + (2\alpha - 4\alpha^3) \exp\left(-\frac{1}{4\alpha^2}\right) \right] \quad (7)$$

The GGA enhancement factors $F_{\text{x}}^{\text{PBE}}$ and $F_{\text{x}}^{\text{RPBE}}$ are taken from the PBE¹⁶ and RPBE¹⁷ functionals, and the kinetic energy density enhancement factors for the exchange have the same form as those in the M08¹⁵ functionals

$$f_1(w) = \sum_{i=0}^m a_i^{\text{x}} w^i \quad (8)$$

$$f_2(w) = \sum_{i=0}^m b_i^{\text{x}} w^i \quad (9)$$

where

$$w = \frac{y-1}{y+1} \quad -1 \leq w \leq 1 \quad (10)$$

$$y = \frac{\tau^{\text{UEG}}}{\tau} \quad (11)$$

with

$$\tau^{\text{UEG}} = \frac{3}{10}(3\pi^2)^{2/3}\rho^{5/3} \quad (12)$$

and

$$\tau = \frac{1}{2} \sum_{i=1}^n |\nabla\psi_i|^2 \quad (13)$$

The nonlocal HF exchange energy is calculated from the occupied spin-orbitals $\psi_{i\sigma}$ using the range-separated Coulomb

operator, as

$$E_{\text{x}}^{\text{LR-HF}} = \frac{1}{2} \sum_{\sigma} \sum_{i,j}^{\text{occ.}} \int \text{d}\mathbf{r}_1 \text{d}\mathbf{r}_2 \, \psi_{i\sigma}^*(\mathbf{r}_1) \psi_{j\sigma}^*(\mathbf{r}_1) \frac{\text{erf}(\omega r_{12})}{r_{12}} \psi_{i\sigma}(\mathbf{r}_2) \psi_{j\sigma}(\mathbf{r}_2) \quad (14)$$

notice that the M11 functional contains a portion of short-range Hartree–Fock exchange equal to $(X/100)(E_{\text{x}}^{\text{HF}} - E_{\text{x}}^{\text{LR-HF}})$, but the portion of Hartree–Fock exchange is 100% at large electronic separation.

Correlation. The M11 correlation has the same functional form as the M08 correlation.¹⁵ In particular, the kinetic energy density enhancement factors are

$$f_3(w) = \sum_{i=0}^m a_i^{\text{c}} w^i \quad (15)$$

$$f_4(w) = \sum_{i=0}^m b_i^{\text{c}} w^i \quad (16)$$

Constraints. As in the development of the M08-SO functional¹⁵ (which is a global-hybrid meta-GGA) and of our recent SOGGA11 functional¹⁸ (which is a GGA), we elected to enforce two physical constraints on exchange and the same two on correlation, in particular, we require them to go to the correct uniform electron gas (UEG) limit and to have the correct second-order (SO) term in the density gradient expansion (that is, the correct coefficient of s^2). The enforcement of the UEG on both the exchange and the correlation is satisfied by

$$\left(1 - \frac{X}{100}\right)(a_0^{\text{x}} + b_0^{\text{x}}) + \frac{X}{100} = 1 \quad (17)$$

$$a_0^{\text{c}} = 1 \quad (18)$$

while the conditions for the SO constraints derive from the gradient expansion of the functional form (see, e.g., eq 18 in ref 15) and are

$$\left(1 - \frac{X}{100}\right)a_0^{\text{x}}\mu^{\text{PBE}} + \left(\frac{X}{100} + \left(1 - \frac{X}{100}\right)b_0^{\text{x}}\right)\mu_2 - \frac{5}{54}\left(1 - \frac{X}{100}\right)(a_1^{\text{x}} + b_1^{\text{x}}) = \frac{10}{81} \quad (19)$$

$$a_1^{\text{c}} = 0 \quad (20)$$

with $\mu^{\text{PBE}} = 0.21951$ and $\mu_2 = 10/81$.

Following Becke in the B99 meta-GGA functional,¹⁹ we also enforce two constraints at the extremes of the kinetic-energy-dependent term for the exchange. At the tails of the density ($w = -1$) and at the bond saddle points ($w = 1$), the kinetic energy density is no longer an accurate measure of delocalization, and the contribution given by the kinetic-energy-dependent term should reduce to the more physical description of the system given by GGA. The original idea of Becke has also found practical applications in the τHCTH^{20} and BMK^{21} functionals. These conditions are enforced on the coefficients of the M11 functional by

$$f_1(w = -1) + f_2(w = -1) = \sum_{i'=0}^{m/2} (a_{2i'}^{\text{x}} - a_{2i'+1}^{\text{x}} + b_{2i'}^{\text{x}} - b_{2i'+1}^{\text{x}})(1 - Y) = 1 \quad (21)$$

$$f_1(w = 1) + f_2(w = 1) = \sum_{i=0}^m (a_i^{\text{x}} + b_i^{\text{x}})(1 - Y) = 1 \quad (22)$$

We also checked that the curve of the meta-GGA energy density remains physically positive by plotting it at various times during the optimization process. This showed that it was not necessary to enforce a positivity condition on the M11 exchange enhancement factor because it remained positive without forcing it to do so.

Databases. Many databases have been compiled and used in our group for the optimization and testing of new density functionals, and we recently¹⁸ reorganized them into a database called BC322, which denotes a “broad chemistry” database with 322 data. This database is used here, with the addition of a database of 10 difficult cases for DFT. Because BC322 is described in detail in the original reference,¹⁸ we simply summarize its main features here. BC322 emphasizes main-group and transition-metal thermochemistry, kinetics, π interactions, and noncovalent interactions. It is divided into 15 subdatabases: MGAE109/05²² for main-group atomization energies, ISOL6²³ for isomerization energies of large organic molecules, IP13/03^{22,24–26} for ionization potentials, EA13/03^{22,24–26} for electron affinities, PA8²⁷ for proton affinities, ABDE4/05^{22,28,29} and ABDEL8¹⁸ for alkyl bond dissociation reaction energies, HC7/11 for hydrocarbons, HTBH38/08^{22,30,31} and NHTBH38/08^{22,30,31} for hydrogen-transfer and non-hydrogen-transfer barrier heights, π TC13^{24,27,28} for π -system thermochemistry, NCCE31/05^{25,32} for noncovalent complexes, AE17^{33,34} for atomic energies, SRMBE12¹⁸ for single-reference bond dissociation energies involving metallic elements, and MRMBE5¹⁸ for multireference bond energies involving metallic elements. Note that “single-reference” and “multi-reference” are qualitative descriptors denoting, respectively, small and large amounts of near-degeneracy correlation energy (also called static correlation energy) in the bond under consideration, as explained elsewhere.³⁵ The DC10 database³³ for 10 cases previously found to be difficult for DFT is added to BC322 to form the BC332 database, composed of a total of 16 subdatabases.

Geometries, Basis Sets, Relativistic Effects, Software. The MG3S basis²⁶ was used for MGAE109/05, IP13/03, EA13/03, PA8/06, ABDE4/05, ABDEL8, π TC13, HTBH38/08, NHTBH38/08, NCCE31/05, DC10, and AE17, the 6-311+G(2df,2p) basis³⁶ was used for HC7/11, and the MG3SXP basis¹⁵ was used for ISOL6/11. All energetic databases except SRMBE12 and MRMBE5 were calculated with single-point energy calculations at standard¹⁸ geometries. Geometries for the molecules in SRMBE12 and MRMBE5 were optimized consistently with each level of theory, using the def2-TZVP basis³⁷ set.

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 were taken into account by using the relativistic effective core potential of the def2-TZVP basis set. The vector relativistic effect was included by adding spin–orbit coupling to atoms and open-shell molecules for which it is nonzero, as described previously.²⁸

All calculations in this Letter were performed with a locally modified version of the Gaussian 09 program,³⁸ using the ultrafine (99,590) Lebedev grid and allowing breaking of the symmetry of the wave function in order to converge to the stable broken-symmetry solution (through the STABLE=OPT Gaussian keyword).

Table 1. Optimized Parameters for the M11 Functional

	exchange	correlation
a_0	$-3.2167657 \times 10^{-1}$	1.0000000
a_1	-2.4308864×10	0.0000000
a_2	2.0665531×10	-3.8933250
a_3	5.4213018×10	-2.1688455
a_4	-9.0843653×10	9.3497200
a_5	2.7229076×10	-1.9845140×10
a_6	-1.2146429×10^1	2.3455253
a_7	-2.7703674×10^2	7.9246513×10
a_8	-2.5952372	9.6042757
a_9	9.6336036×10	-6.7856719×10
a_{10}	-2.3551431×10	-9.1841067
b_0	1.3216766	7.2239798×10^{-1}
b_1	2.3975165×10	4.3730564×10^{-1}
b_2	-2.2377326×10	-1.6088809×10
b_3	-5.1298744×10	-6.5542437×10
b_4	1.0333491×10^2	3.2057230×10
b_5	-3.9791060×10	1.8617888×10^2
b_6	-1.7966668×10	2.0483468×10
b_7	2.8802925×10^2	-7.0853739×10
b_8	3.2403716×10	4.4483915×10
b_9	-9.7347140×10	-9.4484747×10
b_{10}	1.3076588×10	-1.1459868×10^2
X	42.8	
ω	0.25	

Optimization. The optimization of M11 is performed by minimizing a training function, F , defined by

$$\begin{aligned}
 F = & w_1 R_p(\text{MGAE109/05}) + w_2 R(\text{ISOL6/11}) \\
 & + w_3 R(\text{IP13/03}) + w_4 R(\text{EA13/03}) \\
 & + w_5 R(\text{PA8/06}) + w_6 R(\text{ABDE4/05}) \\
 & + w_7 R(\text{ABDEL8}) + w_8 R(\text{HC7/11}) \\
 & + w_9 R(\pi\text{TC13}) + w_{10} R(\text{HTBH38/08}) \\
 & + w_{11} R(\text{NHTBH38/08}) \\
 & + w_{12} R(\text{NCCE31/05}) + w_{13} R(\text{DC10}) \\
 & + w_{14} R(\text{AE17}) + w_{15} R(\text{SRMBE12}) \\
 & + w_{16} R(\text{MRMBE5})
 \end{aligned} \quad (23)$$

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

Weights are chosen by comparing the performance of the new functional to that of M08-HX, which was, on average, the best previous performer for BC332. The weights that we used are those that minimize the value of the training function (eq 23) and, at the same time, provide performances comparable or better than that of M08-HX for each database. It is important to note that 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 training process that are used to get good across-the-board performance for the various subdatabases.

We studied the convergence of the results as a function of the number of terms in the expansion series of the enhancement factors in eqs 8, 9, 15, and 16, as well as the behavior of the global

Table 2. Mean Unsigned Errors (kcal/mol) for the BC332 Database

	PBE	SOGGA11	B3LYP	B97-3	ω B97X	ω B97X-D	M06-L	M05	M05-2X	M06	M06-2X	M06-HF	M08-HX	M08-SO	M11		
# parameters	0	18	3	19	33	33	38	22	22	38	38	38	47	44	38		
X	0	0	20	26.93	15.77–100	22.2–100	0	28	56	27	54	100	52.23	56.79	42.8–100		
ω					0.3	0.2									0.25		
database	w_n^a	GGA		hybrid GGA		RSH-GGA		meta-GGA		hybrid meta-GGA						RSH meta-GGA	
		PBE	SOGGA11	B3LYP	B97-3	ω B97X	ω B97X-D	M06-L	M05	M05-2X	M06	M06-2X	M06-HF	M08-HX	M08-SO	M11	
MGAE109/05 ^b	30	2.99	1.64	0.94	0.62	0.48	0.50	0.85	0.55	0.51	0.60	0.43	0.68	0.68	0.62	0.51	
ISOL6/11	10	1.98	1.73	2.61	2.07	1.55	1.15	2.76	2.75	1.22	1.27	1.53	2.46	0.59	1.19	1.10	
IP13/03	4	3.62	4.74	4.76	3.54	2.82	3.02	3.08	2.82	3.55	3.28	2.56	3.80	3.42	3.58	3.64	
EA13/03	2	2.27	5.23	2.33	2.13	2.01	1.86	3.83	2.97	2.04	1.85	2.14	3.31	1.32	2.72	0.89	
PA8/06	5	1.34	2.11	1.02	2.54	1.51	2.36	1.88	2.26	1.42	1.84	1.65	2.28	1.08	1.64	1.03	
ABDE4/05	1	4.09	5.00	8.73	4.74	3.70	3.73	5.54	5.98	2.45	2.84	2.12	4.43	2.67	2.51	2.45	
ABDEL8	5	7.16	7.89	10.40	7.70	4.82	4.92	8.85	8.78	2.73	4.72	2.69	4.56	2.87	3.88	3.48	
π TC13	1	6.01	7.61	6.06	7.10	3.94	5.82	6.52	5.18	3.05	4.08	1.51	1.92	1.98	1.87	2.12	
HTBH38/08	6	9.31	6.57	4.23	2.28	2.01	2.36	4.15	1.94	1.26	1.98	1.14	2.07	0.72	1.07	1.30	
NHTBH38/08	6	8.42	4.32	4.55	1.38	2.89	3.74	3.81	2.07	1.81	2.33	1.22	2.53	1.22	1.23	1.28	
NCCE31/05	10	1.24	1.28	0.96	0.98	0.50	0.32	0.58	0.49	0.28	0.41	0.29	0.41	0.35	0.37	0.26	
AE17	1	54.44	6.99	13.62	9.24	3.06	3.23	3.86	9.17	5.77	6.85	6.18	3.68	6.54	10.54	5.15	
HC7/11	2	3.97	6.26	16.80	7.58	6.77	4.63	3.35	7.71	3.64	2.78	2.15	2.29	4.89	4.60	3.74	
DC10	1	39.22	30.71	20.66	18.67	9.92	10.39	19.76	16.15	10.73	9.45	10.46	15.63	9.60	10.87	8.03	
SRMBE12	6	3.87	4.32	2.88	3.59	3.98	2.76	3.41	3.09	3.86	2.77	3.90	6.98	3.36	2.87	3.67	
MRMBE5	1	6.74	7.12	14.71	16.75	15.09	16.79	6.95	9.85	29.28	13.20	30.28	53.20	16.83	16.05	14.14	
BC332		8.18	4.60	4.35	3.13	2.30	2.48	3.24	2.88	2.31	2.30	2.11	3.17	1.98	2.32	1.84	

^aData in this column are the relative weights (un-normalized) of each database, w_n , in the M11 training function (eq 23); these weights are not used for computing the mean errors reported in the table. ^bErrors for MGAE109/05 are reported on a per bond basis as in all previous references; therefore, they are effectively mean unsigned errors in bond dissociation energies.

functional as a function of the weights by using post-SCF calculations. We found that good convergence is achieved at $m = 10$ for both the exchange and the correlation, leading to a total of 44 parameters, 4 less than were used in the M08 functionals. The number of empirically fitted parameters is further reduced by the physical constraints that we enforce, bringing the total to 38. To draw a comparison with some of the other functionals in the Minnesota family, M05 has 22 fitted parameters, M06 has 38, M08-SO has 44, and M08-HX has 47.

After the preliminary analysis at the post-SCF level, the 38 free coefficients of M11 were optimized self-consistently at fixed values of ω , between 0 and 0.5. We found that the value of the global MUE remains reasonably constant over $0.2 \leq \omega \leq 0.3$, and we chose the intermediate point at $\omega = 0.25$ as the final value for the M11 functional. The percentage of full-range HF exchange, X, has been also optimized for each step. The final values for all parameters in M11 are in Table 1. FORTRAN routines for the M11 functional are included in the Supporting Information and are also freely available on our webpage within the Minnesota Functional Module.³⁹ The weights used in the training function for the optimization of M11 are reported in the first column of Table 2.

The meta-GGA exchange enhancement factor as a function of the kinetic energy density variable w is plotted in Figure 1 for $s = 0$, and it is compared to that of other common meta-GGA functionals. In the plots of Figure 1, the UEG corresponds to $w = 0$, while the extremes at $w = -1$ and $w = 1$ represent the exponential tails and the bond saddle points, respectively. All functional forms respect the UEG at $w = 0$. As explained above,

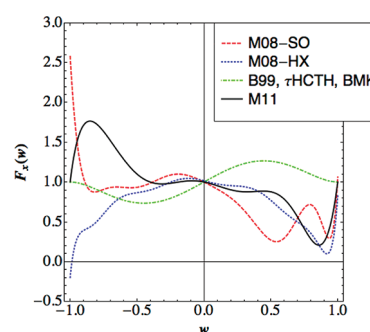


Figure 1. Meta-GGA exchange enhancement factors at $s = 0$ for six functionals.

we constrained M11 to be physical at $w = \pm 1$, but we see that the M08 functionals have very different behavior at $w = -1$. Neither M08 functional appears trustworthy at $w = -1$, and M08-HX has an unphysical negative value there. At $w = 1$, the differences between the functionals are smaller. This might indicate that bond saddle points are more important than exponential tails for predicting chemical data; therefore, the optimization does not concern itself with getting the $w = -1$ limit correct.

Performance. We compare the performance of the M11 functional with those of common GGA and meta-GGA approximations in Table 2, which shows mean unsigned errors (MUEs) for BC332 and its subdatabases. The considered functionals are PBE¹⁶ and SOGGA11¹⁸ (GGA functionals), B3LYP^{40–42} and B97-3⁴³ (hybrid GGAs), ω B97X¹⁴ and ω B97X-D⁴⁴ (RSH-GGAs),

Table 3. Excitation Energies (eV) and Mean Unsigned Errors (eV) Relative to Reference Data for the CTS8 Database^a

molecule	PBE	SOGGA11	B3LYP	B97-3	ω B97X	ω B97X-D	M06-L	M05	M05-2X	M06	M06-2X	M06-HF	M08-HX	M08-SO	M11	ref ^b
tetracene	2.15	2.15	2.41	2.51	2.92	2.79	2.27	2.46	2.74	2.42	2.75	3.04	2.76	2.71	2.92	2.88 ^c
NH ₃ ...F ₂	0.11	0.11	2.22	3.02	6.2	5.04	0.76	2.59	5.38	2.63	5.49	9.36	5.27	5.48	6.43	9.46 ^d
C ₂ H ₄ ...C ₂ F ₄	5.13	4.93	7.03	7.61	10.83	9.91	5.69	7.55	9.6	7.58	9.36	12.62	9.21	4.72	10.93	12.63 ^e
MUE (CTES3)	5.86	5.93	4.44	3.94	1.70	2.41	5.42	4.12	2.42	4.11	2.46	0.09	2.58	4.02	1.59	
11- <i>Z</i> -cis-Retinal																
S ₁	1.94	1.93	2.30	2.27	2.54	2.54	2.05	2.26	2.44	2.34	2.45	2.92	2.42	2.38	2.49	2.10 ^f
S ₂	2.68	2.67	3.04	3.17	3.86	3.72	2.84	3.12	3.56	3.15	3.49	4.27	3.54	3.48	3.79	3.30 ^f
11- <i>Z</i> -cis-7,8-Dihydroretinal																
S ₁	0.93	0.96	1.54	1.79	3.17	3.05	1.04	1.82	2.83	1.81	2.73	3.20	2.68	2.78	3.11	2.62 ^f
S ₂	2.12	2.18	3.07	3.17	3.99	3.44	2.42	3.13	3.28	3.13	3.23	4.61	3.20	3.20	3.91	3.03 ^f
S ₃	2.44	2.52	3.22	3.51	5.27	4.99	2.75	3.42	4.64	3.50	4.48	5.30	4.46	4.57	5.21	4.40 ^f
MUE (retinals)	1.07	1.04	0.55	0.43	0.68	0.46	0.87	0.44	0.26	0.44	0.19	0.97	0.17	0.19	0.61	
MUE (CTS8)	2.87	2.87	2.01	1.75	1.06	1.19	2.58	1.82	1.07	1.82	1.04	0.64	1.07	1.63	0.98	

^a All calculations for CTS8 are performed using the 6-31++G(d,p) basis set as used in ref 47. Geometries are taken from previous work^{45,46} and are presented in the Supporting Information. ^b Reference data. ^c Experimental, ref 48. ^d SAC-CI/6-31+G(d,p), ref 45. ^e SAC-CI/6-31G*, ref 49. ^f RI-CC2/def-TZVP, ref 50.

and all eight previous Minnesota functionals, M05,²⁴ M05-2X,²² M06-L,²⁸ M06,³³ M06-2X,³³ M06-HF,⁴⁵ M08-SO,¹⁵ and M08-HX.¹⁵

The overall performance of each functional is evaluated by calculating the MUE over the total set of 332 data in the training set and is reported in the last row of Table 2. In terms of overall performance, M11 is the best functional of all those considered. From the results in Table 2, it is clear that GGA functionals cannot provide consistently good results for all components of such a broad database. SOGGA11 is an improvement over PBE, and it is interesting to note that SOGGA11 has similar overall results as the very popular B3LYP hybrid functional, but it achieves this with no HF exchange. However, the addition of carefully optimized HF exchange, as in B97-3, lowers the MUE by 32%. M11 then lowers the MUE relative to B97-3 by 42%.

M11 is clearly superior to both SOGGA11 and B3LYP. Not only is M11's total MUE lower, but its MUE is lower or comparable for every subdatabase except one. The one exception is the multireference metal bond energy database, but this was expected because it has been known for some time³⁵ that one cannot obtain good results on multireference systems with a high percentage *X* of Hartree–Fock exchange. It is pleasantly surprising that M11 with *X* rising from 42.8 at small interelectronic distances to 100 at long range does about as well for the multireference metal bond energy database as B3LYP with a much smaller *X* of 20. B3LYP is still widely applied to transition-metal systems, although we would recommend M06-L, SOGGA11, or M05 be used instead for systems with large multireference character.

The advantage of including kinetic energy density is clear from the comparison between the ω B97X and ω B97X-D RSH-GGAs and the M11 RSH-meta-GGA. M11 is better than both RSH-GGAs for all databases except IP13/03 and AE17, for which performances are only slightly worse.

The advantage of the range separation for meta-GGA hybrids can be ascertained by comparing the performance of M11 to that of M08-SO; these two functionals share the same DFT functional form (except for the range separation) and two important constraints (UEG and SO). M11 is, on average, better than M08-SO for the entire broad chemistry set, and it is also better for almost all of the considered databases, with only a few exceptions, in which cases, M08-SO is only slightly superior.

As compared to the M06-2X and the M08-HX functionals, which have both been very successful for barrier heights and noncovalent interactions, it is noteworthy that M11 competes well with them in those categories (HTBH38/08, NHTBH38/08, and NCCE31/05). In particular for noncovalent interactions, M11 performs better than all other functionals, and the results are even more encouraging if we consider some significant subsets of this database (see Supporting Information for a detailed table). For example, M11 has a MUE of only 0.09 kcal/mol for the weak interactions subset, a value that strongly outperforms all previous Minnesota functionals. All other subsets of NCCE31/05 also show uncommonly good results, with MUEs of 0.37 kcal/mol for hydrogen bonding, 0.30 kcal/mol for charge-transfer (CT) complexes, 0.33 kcal/mol for dipole interactions, and 0.22 kcal/mol for π – π stacking.

Further Validation. We next tested the new functional on additional databases. One of the advantages of having an RSH functional with 100% HF exchange at large interelectronic separations is that it should improve performance over most global hybrids in time-dependent DFT (TDDFT) calculations of CT excited states. To test M11 for such problems, we created a new database for CT spectroscopy called CTS8, which consists of three singlet \rightarrow singlet CT excitations energies from the previous CTES3 database⁴⁵ and five singlet \rightarrow singlet electronic excitation energies with varying amounts of CT for two retinals. CTES3 contains CT excitation energies for tetracene molecules, the NH₃...F₂ complex (at 6 Å), and the C₂H₄...C₂F₄ (at 8 Å) complex. We added two excitation energies for 11-*Z*-cis-retinal and three for 11-*Z*-cis-7,8-dihydroretinal, from refs 46 and 47. The CT excitations of the complexes in the CTES3 database are characterized by almost no overlap, while the retinal CT excitations can be classified in the intermediate range. TDDFT results for CTS8 are presented in Table 3. The overall performance of M11 for CTS8 is quite satisfying; M11 and M06-HF are the only functionals with MUEs below 1 eV. M06-HF has a lower MUE because of its excellent performance for the two cases with almost no overlap, but it is not as successful as M11 for general applications, with a MUE for BC322 worse than that of M11 by about 75%. Moreover, as also previously shown,⁴⁶ the performance of M06-HF for excitation with intermediate spatial overlap is not as

Table 4. Mean Signed and Unsigned Errors (kcal/mol) for the Noncovalent Binding Energies of the S22A Database^a

functional	MSE	MUE
PBE	−2.54	2.57
SOGGA11	−1.16	1.54
B3LYP	3.77	3.77
B97-3	1.06	1.26
ω B97X	0.53	0.87
ω B97X-D	0.17	0.23
M06-L	−0.77	0.80
M05	−2.05	2.07
M05-2X	−0.60	0.79
M06	−1.06	1.06
M06-2X	−0.21	0.40
M06-HF	0.01	0.62
M08-HX	−0.15	0.47
M08-SO	−0.24	0.48
M11	−0.21	0.44

^a Calculations for this database were performed with the 6-311+G-(3df,2p) basis set^{36,53,54} with counterpoise corrections^{55,56} for the basis set superposition error.

good as that of some other hybrid functionals, and here, we show that that includes M11. Common local functionals and global hybrids perform very poorly for the CTES3 subset, with the best MUE of 2.42 eV for M05-2X being 54% worse than that for M11. One would not want to use any of these functionals except M06-HF for pure CT transitions, but a small error for the CT cases is also desirable because many excitations that one does want to treat have partial CT character. Aside from M11, the only other functionals to show good balance for the whole CTS8 database are ω B97X and ω B97X-D, which are both RSH-GGAs. The performances of ω B97X and ω B97X-D on BC322, however, are about 30% worse than that for M11.

The next database that we consider to validate the new functional is the popular S22 database of Jurecka et al.,⁵¹ updated to S22A by using the more accurate reference values of Takatani et al. (see Table 4).⁵² The top performer for this database is the ω B97X-D functional, which includes post-SCF molecular mechanics corrections. M06-2X is second best, and M11 is right behind it, with comparable performance; the M08 functionals also perform well. All other meta-GGA functionals fare worse than the top performers by at least 20%, while GGA and global-hybrid GGA functionals are off by a much larger factor.

Concluding Remarks. In this work, we optimized a new range-separated hybrid meta-GGA functional correct to second order in both the exchange and the correlation. The new functional is called M11, and it is the latest addition to the Minnesota family of functionals.

We compared the performance of M11 to that of several functionals for a broad chemistry database of 332 data. For the ionization potential subdatabase, the result is better than SOGGA11 and B3LYP and almost as good as PBE, M06-L, M05-2X, and both M08 functionals but 42% worse than the best functional. For the multireference bond energy subdatabase, the result is much worse than functionals with $X = 0$, but it is comparable to B3LYP and better than previous range-separated hybrids or than any global hybrid with $X > 30$. For the other 14 subdatabases, M11 shows either the best performance or comes

close it, and, when averaged over all of the data, because of this good across-the-board performance, it has the lowest mean unsigned error. As compared to most other functionals, the accuracy is particularly good for main-group atomization energies, proton affinities, electron affinities, alkyl bond dissociation energies, barrier heights, noncovalent interaction energies, and difficult cases.

The results obtained with the broad chemistry training set and the specialized databases show that M11 shows significant improvement as compared to previous functionals.

■ ASSOCIATED CONTENT

S Supporting Information. Mean signed errors, maximum errors, performance for subset databases, geometries for CTS8, and a FORTRAN program for M11. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: truhlar@umn.edu.

■ ACKNOWLEDGMENT

We are grateful to Yan Zhao for many helpful and important contributions to this research. This work was supported in part by the Air Force Office of Scientific Research by Grant No. FA9550-11-0078.

■ REFERENCES

- (1) Kohn, W.; Becke, A.; Parr, Y. Density Functional Theory of Electronic Structure. *J. Phys. Chem.* **1996**, *100*, 12974.
- (2) Cramer, C. J.; Truhlar, D. G. Density Functional Theory for Transition Metals and Transition Metal Chemistry. *Phys. Chem. Chem. Phys.* **2009**, *11*, 10757.
- (3) Perdew, J. P.; Ruzsinszky, A.; Tao, J.; Staroverov, V. N.; Scuseria, G. E.; Csonka, G. I. Prescription for the Design and Selection of Density Functional Approximations: More Constraint Satisfaction with Fewer Fits. *J. Chem. Phys.* **2005**, *123*, 062201.
- (4) Kohn, W.; Sham, L. Self-Consistent Equations Including Exchange and Correlation Effects. *Phys. Rev.* **1964**, *140*, 1133.
- (5) Becke, A. D. A New Mixing of Hartree–Fock and Local Density-Functional Theories. *J. Chem. Phys.* **1992**, *98*, 1372–1377.
- (6) Zhao, Y.; Lynch, B.; Truhlar, D. G. Doubly Hybrid Meta DFT: New Multi-Coefficient Correlation and Density Functional Methods for Thermochemistry and Thermochemical Kinetics. *J. Phys. Chem. A* **2003**, *108*, 4786–4791.
- (7) Toulouse, J.; Colonna, F.; Savin, A. Long-Range–Short-Range Separation of the Electron–Electron Interaction in Density-Functional Theory. *Phys. Rev. A* **2004**, *70*, 062505.
- (8) Heyd, J.; Scuseria, G. E. Assessment and Validation of a Screened Coulomb Hybrid Density Functional. *J. Chem. Phys.* **2003**, *120*, 7274–7280.
- (9) Yanai, T.; Tew, D.; Handy, N. A New Hybrid Exchange–Correlation Functional Using the Coulomb-Attenuating Method (CAM-B3LYP). *Chem. Phys. Lett.* **2004**, *393*, 51–57.
- (10) Gerber, I.; Angyan, J. Hybrid Functional with Separated Range. *Chem. Phys. Lett.* **2005**, *415*, 100–105.
- (11) Vydrov, O. A.; Scuseria, G. E. Assessment of a Long-Range Corrected Hybrid Functional. *J. Chem. Phys.* **2006**, *125*, 234109.
- (12) Song, J.-W.; Tokura, S.; Sato, T.; Watson, M. A.; Hirao, K. An Improved Long-Range Corrected Hybrid Exchange–Correlation Functional Including a Short-Range Gaussian Attenuation (LCgau-BOP). *J. Chem. Phys.* **2007**, *127*, 154109.

- (13) Goll, E.; Werner, H.-J.; Stoll, H. Short-Range Density Functionals in Combination with Local Long-Range Ab Initio Methods: Application to Non-Bonded Complexes. *Chem. Phys.* **2008**, *346*, 257–265.
- (14) Chai, J.-D.; Head-Gordon, M. Systematic Optimization of Long-Range Corrected Hybrid Density Functionals. *J. Chem. Phys.* **2008**, *128*, 084106.
- (15) Zhao, Y.; Truhlar, D. G. Exploring the Limit of Accuracy of the Global Hybrid Meta Density Functional for Main-Group Thermochemistry, Kinetics, and Noncovalent Interactions. *J. Chem. Theory Comput.* **2007**, *4*, 1849–1868.
- (16) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1995**, *77*, 3865–3868.
- (17) Hammer, B.; Hansen, L.; Norskov, J. Improved Adsorption Energetics within Density-Functional Theory Using Revised Perdew–Burke–Ernzerhof Functionals. *Phys. Rev. B* **1999**, *59*, 7413–7421.
- (18) Peverati, R.; Zhao, Y.; Truhlar, D. G. Generalized Gradient Approximation That Recovers the Second-Order Density-Gradient Expansion with Optimized Across-the-Board Performance. *J. Phys. Chem. Lett.* **2011**, *2*, 1991–1997.
- (19) Becke, A. D. Simulation of Delocalized Exchange by Local Density Functionals. *J. Chem. Phys.* **1999**, *112*, 4020–4026.
- (20) Boese, A. D.; Handy, N. C. New Exchange–Correlation Density Functionals: The Role of the Kinetic-Energy Density. *J. Chem. Phys.* **2001**, *116*, 9559–9569.
- (21) Boese, A.; Martin, J. Development of Density Functionals for Thermochemical Kinetics. *J. Chem. Phys.* **2004**, *121*, 3405–3416.
- (22) Zhao, Y.; Schultz, N. E.; Truhlar, D. G. Design of Density Functionals by Combining the Method of Constraint Satisfaction with Parametrization for Thermochemistry, Thermochemical Kinetics, and Noncovalent Interactions. *J. Chem. Theory Comput.* **2005**, *2*, 364–382.
- (23) Luo, S.; Zhao, Y.; Truhlar, D. G. Validation of Electronic Structure Methods for Isomerization Reactions of Large Organic Molecules. *Phys. Chem. Chem. Phys.* **2011**, *13*, 13683–13689.
- (24) Zhao, Y.; Schultz, N. E.; Truhlar, D. G. Exchange–Correlation Functional with Broad Accuracy for Metallic and Nonmetallic Compounds, Kinetics, and Noncovalent Interactions. *J. Chem. Phys.* **2005**, *123*, 161103.
- (25) Zhao, Y.; Truhlar, D. G. Design of Density Functionals That Are Broadly Accurate for Thermochemistry, Thermochemical Kinetics, and Nonbonded Interactions. *J. Phys. Chem. A* **2005**, *109*, 5656–5667.
- (26) Lynch, B. J.; Zhao, Y.; Truhlar, D. G. Effectiveness of Diffuse Basis Functions for Calculating Relative Energies by Density Functional Theory. *J. Phys. Chem. A* **2003**, *107*, 1384–1388.
- (27) Zhao, Y.; Truhlar, D. G. Assessment of Density Functionals for π Systems: Energy Differences between Cumulenes and Polyynes; Proton Affinities, Bond Length Alternation, and Torsional Potentials of Conjugated Polyenes; and Proton Affinities of Conjugated Schiff Bases. *J. Phys. Chem. A* **2006**, *110*, 10478–10486.
- (28) Zhao, Y.; Truhlar, D. G. A New Local Density Functional for Main-Group Thermochemistry, Transition Metal Bonding, Thermochemical Kinetics, and Noncovalent Interactions. *J. Chem. Phys.* **2005**, *125*, 194101.
- (29) Izgorodina, E.; Coote, M.; Radom, L. Trends in R–X Bond Dissociation Energies (R = Me, Et, *i*-Pr, *t*-Bu; X = H, CH₃, OCH₃, OH, F): A Surprising Shortcoming of Density Functional Theory. *J. Phys. Chem. A* **2005**, *109*, 7558–7566.
- (30) Zhao, Y.; Lynch, B. J.; Truhlar, D. G. Multi-Coefficient Extrapolated Density Functional Theory for Thermochemistry and Thermochemical Kinetics. *Phys. Chem. Chem. Phys.* **2005**, *7*, 43–52.
- (31) Zhao, Y.; González-García, N.; Truhlar, D. G. Benchmark Database of Barrier Heights for Heavy Atom Transfer, Nucleophilic Substitution, Association, and Unimolecular Reactions and Its Use to Test Theoretical Methods. *J. Phys. Chem. A* **2005**, *109*, 2012–2018.
- (32) Zhao, Y.; Truhlar, D. G. Benchmark Databases for Nonbonded Interactions and Their Use To Test Density Functional Theory. *J. Chem. Theory Comput.* **2005**, *1*, 415–432.
- (33) Zhao, Y.; Truhlar, D. G. The M06 Suite of Density Functionals for Main Group Thermochemistry, Thermochemical Kinetics, Noncovalent Interactions, Excited States, and Transition Elements: Two New Functionals and Systematic Testing of Four M06-Class Functionals and 12 Other Functionals. *Theor. Chem. Acc.* **2008**, *120*, 215–241.
- (34) Chakravorty, S.; Gwaltney, S.; Davidson, E.; Parpia, F.; Fischer, C. Ground-State Correlation Energies for Atomic Ions with 3 to 18 Electrons. *Phys. Rev. A* **1993**, *47*, 3649–3670.
- (35) Schultz, N. E.; Zhao, Y.; Truhlar, D. G. Density Functionals for Inorganometallic and Organometallic Chemistry. *J. Phys. Chem. A* **2005**, *109*, 11127–11143.
- (36) Radom, L.; Schleyer, P. R.; Pople, J. A.; Hehre, W. J. *Ab Initio Molecular Orbital Theory*, 1st ed.; Wiley: New York, 1986.
- (37) Weigend, F.; Ahlrichs, R. Balanced Basis Sets of Split Valence, Triple Zeta Valence and Quadruple Zeta Valence Quality for H to Rn: Design and Assessment of Accuracy. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297.
- (38) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; et al. *Gaussian 09*, revision A.1; Gaussian, Inc.: Wallingford, CT, 2009.
- (39) *Minnesota Functional Module*, version 1.4. <http://comp.chem.umn.edu/mfm> (2011).
- (40) Becke, A. D. Density-Functional Exchange-Energy Approximation with Correct Asymptotic-Behavior. *Phys. Rev. A* **1988**, *38*, 3098–3100. Becke, A. D. Density-Functional Thermochemistry. 3. The Role of Exact Exchange. *J. Chem. Phys.* **1992**, *98*, 5648–5652.
- (41) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle–Salvetti Correlation-Energy Formula into a Functional of the Electron-Density. *Phys. Rev. B* **1987**, *37*, 785–789.
- (42) Stephens, P.; Devlin, F.; Chabalowski, C.; Frisch, M. J. Ab-Initio Calculation of Vibrational Absorption and Circular-Dichroism Spectra Using Density-Functional Force-Fields. *J. Phys. Chem.* **1993**, *98*, 11623–11627.
- (43) Keal, T.; Tozer, D. Semiempirical Hybrid Functional with Improved Performance in an Extensive Chemical Assessment. *J. Chem. Phys.* **2005**, *123*, 121103.
- (44) Chai, J.-D.; Head-Gordon, M. Long-Range Corrected Hybrid Density Functionals with Damped Atom–Atom Dispersion Corrections. *Phys. Chem. Chem. Phys.* **2007**, *10*, 6615–6620.
- (45) Zhao, Y.; Truhlar, D. G. Density Functional for Spectroscopy: No Long-Range Self-Interaction Error, Good Performance for Rydberg and Charge-Transfer States, and Better Performance on Average than B3LYP for Ground States. *J. Phys. Chem. A* **2005**, *110*, 13126–13130.
- (46) Li, R.; Zheng, J.; Truhlar, D. G. Density Functional Approximations for Charge Transfer Excitations with Intermediate Spatial Overlap. *Phys. Chem. Chem. Phys.* **2010**, *12*, 12697–12701.
- (47) Dwyer, A. D.; Tozer, D. Effect of Chemical Change on TDDFT Accuracy: Orbital Overlap Perspective of the Hydrogenation of Retinal. *Phys. Chem. Chem. Phys.* **2010**, *12*, 2816.
- (48) Biermann, D.; Schmidt, W. Diels-Alder Reactivity of Polycyclic Aromatic Hydrocarbons. 1. Acenes and Benzologs. *J. Am. Chem. Soc.* **1980**, *102*, 3163.
- (49) Tawada, Y.; Tsuneda, T.; Yanagisawa, S.; Yanai, T.; Hirao, K. A Long-Range-Corrected Time-Dependent Density Functional Theory. *J. Chem. Phys.* **2004**, *120*, 8425.
- (50) Zaari, R. R.; Wong, Y. Y. Photoexcitation of 11-Z-cis-7,8-dihydro retinal and 11-Z-cis retinal: A Comparative Computational Study. *Chem. Phys. Lett.* **2009**, *469*, 224.
- (51) Jurečka, P.; Sponer, J.; Cerný, J.; Hobza, P. Benchmark Database of Accurate (MP2 and CCSD(T) Complete Basis Set Limit) Interaction Energies of Small Model Complexes, DNA Base Pairs, and Amino Acid Pairs. *Phys. Chem. Chem. Phys.* **2005**, *8*, 1985.
- (52) Takatani, T.; Hohenstein, E. G.; Malagoli, M.; Marshall, M. S.; Sherrill, C. D. Basis Set Consistent Revision of the S22 Test Set of Noncovalent Interaction Energies. *J. Chem. Phys.* **2009**, *132*, 144104.

(53) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. Self-Consistent Molecular Orbital Methods. XX. A Basis Set for Correlated Wave Functions. *J. Chem. Phys.* **1980**, *72*, 650.

(54) McLean, A. D.; Chandler, G. S. Contracted Gaussian Basis Sets for Molecular Calculations. I. Second Row Atoms, Z=11–18. *J. Chem. Phys.* **1980**, *72*, 5639.

(55) Boys, S. F.; Bernardi, F. Calculation of Small Molecular Interactions by Differences of Separate Total Energies — Some Procedures with Reduced Errors. *Mol. Phys.* **1970**, *19*, 553.

(56) Schwenke, D. W.; Truhlar, D. G. Systematic Study of Basis Set Superposition Errors in the Calculated Interaction Energy of Two HF Molecules. *J. Chem. Phys.* **1985**, *82*, 2418.