M11-L: A Local Density Functional That Provides Improved Accuracy for Electronic Structure Calculations in Chemistry and Physics

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S *Supporting Information*

ABSTRACT: Local approximations to the exchange-correlation functional are of special interest because of their cost advantages and their useful accuracy for efficient calculations on systems (such as many transition metal catalysts) with significant multiconfigurational wave function character. We present a meta-GGA exchange-correlation functional, called M11-L, that employs dual-range local exchange to provide broad accuracy for both single-configurational and multiconfigurational molecules and for solid-state lattice constants. Also notable is the high accuracy (for a local functional) for chemical reaction barrier heights. The mean unsigned error on a broad chemistry database of 338 energetic data is lower than that for any other known functional, even hybrid functionals and range-separated hybrid functionals. This success shows that the dependence of the exchange energy density on interelectronic distance is quite different at short-range and long-range, and it establishes a new standard for the limit of what can be achieved with a local exchange-correlation functional.

SECTION: Molecular Structure, Quantum Chemistry, General Theory
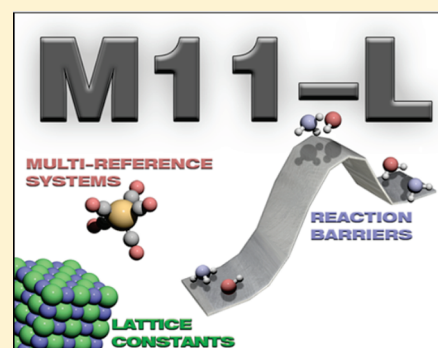
The success of Kohn–Sham density functional theory rests on the accuracy with which one approximates the exchange-correlation functional, often just called the density functional.[1] In the early days of density functional theory, all density functionals were local. Local functionals can depend on a number of variables including the density, the density gradient, the Laplacian of the density, and the orbital-dependent kinetic energy density.

Local functionals that depend on the density only[2] are called local density approximations (LDAs), and they usually do not provide a satisfactory description of chemical bonds. For the general case, including open-shell systems, functions of the density are replaced by functions of the α and β spin densities, and the LDA becomes the local spin density approximation or LSDA, which reduces to the LDA for closed-shell systems. Except for using the general LSDA acronym instead of LDA, we will use the language of closed-shell systems. (The language can be confusing; functionals based on the LSDA are a subset of local density functionals, which include all density functionals whose energy density at a given point depends on functions of the density or the Kohn–Sham orbitals only locally, i.e., only at that single point. Local density functionals that depend on more than the density are sometimes called semilocal.) Going beyond the LSDA by including dependence on the local density gradient yields functionals called generalized gradient approximations (GGAs).[3] The LSDA is usually parametrized based on the uniform-density electron gas (UEG). Enforcing the correct value of the leading (second-order, abbreviated SO) term in the deviation of a GGA from a uniform density did not originally provide satisfactory results for chemical properties, and the

challenge of providing broad accuracy with a local functional correct through SO was solved only recently by using a careful parametrization of a flexible functional form.[4] The majority of GGA functionals currently used in chemistry, however, have a coefficient for the leading nonuniform term for exchange that is about twice the correct one for the exchange. Meta-GGA functionals include independent variables beyond the density and its gradient, in particular the local orbital-dependent kinetic energy density or the local Laplacian of the density, and yield more reliable results. However, functionals that include nonlocal orbital-dependent Hartree–Fock (HF) exchange, the so-called hybrid functionals, have been the most popular choice for chemical applications, and they usually have greater accuracy for chemical problems. ("Hartree–Fock exchange" refers to computing the exchange energy from the Kohn–Sham determinant in the same way that one computes exchange energy from an HF determinant; this is a nonlocal operation.)

We recently presented a very successful hybrid meta-GGA functional,[5] called M11, which uses range separation to include a variable amount of HF exchange: 42.8% at small interelectronic distance u, and 100% at large u. If we compare across-the-board performances, the best hybrid functionals do better than the best corresponding local functionals by a significant amount. For example, the mean unsigned error (MUE) of M11 is about 20% better than the M06-L meta-GGA functional,[6] and our new SOGGA11-X hybrid[7] has an MUE

about 60% smaller than that for the SOGGA11 local functional.[4] Another drawback of local functionals is their inability to accurately describe medium- and long-range charge transfer.

However, local functionals still attract much interest for three reasons: (1) their smaller computational cost, especially for large and extended systems, (2) their ease of implementation, and (3) their better ability to treat systems with multireference character. Note that "single-reference" and "multi-reference" are qualitative descriptors respectively denoting small and large amounts of near-degeneracy correlation energy (also called static correlation energy), as explained elsewhere.[8−10]

In the present Letter we introduce a new local functional form that mixes two optimized meta-GGA exchange functionals at different ranges to provide broad accuracy for a large database of chemical data, including systems with multireference character. Moreover, we enforce important physical constraints, and we validate the new functional's performance for a set of lattice constants.

Databases. Many databases have been compiled and used in our group for the optimization and testing of new density functionals. Here we continue the process of enhancing them. First we expand our previous databases for single-reference and multireference metal bond energies[4] called SRMBE12 and MRMBE5 to respectively include one and five more data. Then we split the MGAE109/11 database of 109 main group atomization energies into two subdatabases according to the B_1 diagnostic,[8] which is the difference of BLYP and B1LYP bond energies at the BLYP geometry. A large value of B_1 (larger than 10 kcal/mol) is considered a difficult case; the difficulty can have any number of causes that make the BLYP GGA (or both) or the B1LYP hybrid GGA especially inaccurate, and we are particularly interested in validating which functionals are accurate enough for such difficult cases.

The new energetic training set is composed of 338 data, and it is called BC338, which denotes a "broad chemistry" database with 338 data. The subdatabases that comprise the training set are small-B_1 and large-B_1 main-group atomization energies (SB1AE97, LB1AE12), single-reference metal bond energies (SRMBE13), multireference bond energies (MRBE10), isomerization energies of large organic molecules (IsoL6),[11] ionization potentials (IP13/03),[12−15] electron affinities (EA13/03),[12−15] proton affinities (PA8),[16] alkyl bond dissociation reaction energies (ABDE4/05[6,13,17] and ABDEL8[4]), hydrocarbons (HC7/11),[4] hydrogen-transfer and non-hydrogen-transfer barrier heights (HTBH38/08,[13,18,19] NHTBH38/08[13,18,19]), π system thermochemistry (πTC13),[6,12,16] noncovalent complexation energies (NCCE31/05),[14,20] difficult cases for DFT (DC10),[21] atomic energies (AE17).[21,22]

Two subsets of BC338 are used for further evaluation of functionals: one that does not include the multireference database and has 328 data, denoted BC328xMR, and one that does not include the 17 atomic energies, denoted BC321xAE. We will also include in the training set database (SSLC15) of solid-state-lattice constants. Details of all the databases used in this work, the basis sets[15,23−26] used for each of them, the geometries, the treatment of relativistic effects, and the software are in the Supporting Information.

Design. The new density functional, called M11-L, is like our recent M11 range-separated functional, except that the computationally expensive HF exchange (the outer-range

exchange of M11) is substituted by an optimized outer-range meta-GGA exchange density functional; the inner range exchange is still of meta-GGA form, but with different parameters than the meta-GGA exchange used at long-range (and also different from those used in M11). A rationale for our new functional form is that the exchange and correlation effects associated with the short-range (SR) and the long-range (LR) portions of the Coulomb interactions depend differently on the independent variables. We incorporate this by using different meta-GGA density functionals for the two ranges. We know of only one previous approximation that makes use of different local approximations for different ranges of u, namely the LRS-ωLDA functional,[27] where the TPSS hole was used to provide a computationally effective local approximation to screen a portion of HF exchange. However, our motivation is different: to find the best performing functional dependence of a range-separated meta-GGA.

We will explain the new functional for a closed-shell system, where we can dispense with the spin labels (the subscripts $\sigma = \alpha, \beta$); the extension to open shells (spin-polarized systems) is standard and is presented in the Supporting Information. We begin by writing the exchange-correlation functional as

$$E_{xc}^{\text{M11-L}} = E_x^{\text{SR-M11}} + E_x^{\text{LR-M11}} + E_c^{\text{M11-L}} \tag{1}$$

and we will formulate it in terms of the density ρ, the reduced density gradient

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

the kinetic energy density

$$\tau = \frac{1}{2}\sum_{i=1}^{n}|\nabla\phi_i|^2 \tag{3}$$

the UEG kinetic energy density

$$\tau^{\text{UEG}} = \frac{3}{10}(3\pi^2)^{2/3}\rho^{5/3} \tag{4}$$

and the reduced variables

$$w = \frac{(\tau^{\text{UEG}}/\tau) - 1}{(\tau^{\text{UEG}}/\tau) + 1}, \quad -1 \leq w \leq 1 \tag{5}$$

and

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

where ω is the range-separation parameter explained elsewhere.[28]

Dual-Range Exchange. The exchange part of the M11-L functional has a short-range part that is the same as used in the M11 functional,

$$E_x^{\text{SR-M11}} = \int d\mathbf{r}\,\varepsilon_x^{\text{SR-LSDA}}(\rho)\{f_1^{\text{SR}}(w)F_x^{\text{PBE}}(s)$$
$$+ f_2^{\text{SR}}(w)F_x^{\text{RPBE}}(s)\} \tag{7}$$

where the GGA enhancement factors F_x^{PBE} and F_x^{RPBE} are taken from the PBE[29] and RPBE[30] functionals, and where, as originally proposed by Chai and Head-Gordon[28] and as used in M11, we introduce the range separation in the

LSDA term as

$$\varepsilon_{\mathbf{x}}^{\text{SR-LSDA}} = -\frac{3}{2}\left(\frac{3}{4\pi}\right)^{1/3}\rho^{4/3}G(\alpha) \tag{8}$$

where

$$G = 1 - \frac{8}{3}\alpha\left[\sqrt{\pi}\ \text{erf}\left(\frac{1}{2\alpha}\right) - 3\alpha + 4\alpha^3\right.$$
$$\left. + (2\alpha - 4\alpha^3)\exp\left(-\frac{1}{4\alpha^2}\right)\right] \tag{9}$$

The long-range part is calculated as

$$E_{\mathbf{x}}^{\text{LR-M11}} = \int d\mathbf{r}\varepsilon_{\mathbf{x}}^{\text{LR-LSDA}}(\rho)\{f_1^{\text{LR}}(w)F_{\mathbf{x}}^{\text{PBE}}(s)$$
$$+ f_2^{\text{LR}}(w)F_{\mathbf{x}}^{\text{RPBE}}(s)\} \tag{10}$$

where

$$\varepsilon_{\mathbf{x}}^{\text{LR-LSDA}} = \varepsilon_{\mathbf{x}}^{\text{LSDA}} - \varepsilon_{\mathbf{x}}^{\text{SR-LSDA}}$$
$$= -\frac{3}{2}\left(\frac{3}{4\pi}\right)^{1/3}\rho^{4/3}\{1 - G(\alpha)\} \tag{11}$$

The kinetic-energy-density enhancement factors for the exchange have the same form as in the M08[23] and M11 functionals:

$$f_1^{\text{SR}} = \sum_{i=0}^{m}a_i^{\text{SR-x}}w^i \tag{12}$$

$$f_2^{\text{SR}} = \sum_{i=0}^{m}b_i^{\text{SR-x}}w^i \tag{13}$$

$$f_1^{\text{LR}} = \sum_{i=0}^{m}a_i^{\text{LR-x}}w^i \tag{14}$$

$$f_2^{\text{LR}} = \sum_{i=0}^{m}b_i^{\text{LR-x}}w^i \tag{15}$$

Correlation. The M11-L correlation has the same functional form as in M08 and M11:

$$E_c^{\text{M11-L}} = \int d\mathbf{r}\rho\varepsilon_c^{\text{LSDA}}(\rho)f_3(w) + \int d\mathbf{r}\rho H^{\text{PBE}}(\rho, s)f_4(w) \tag{16}$$

where $\varepsilon_c^{\text{LSDA}}$ is the correlation energy per electron of the UEG, H^{PBE} is the PBE[29] gradient correction for the correlation, and the kinetic-energy-density enhancement factors for correlation are

$$f_3 = \sum_{i=0}^{m}a_i^{c}w^i \tag{17}$$

$$f_4 = \sum_{i=0}^{m}b_i^{c}w^i \tag{18}$$

Constraints. As in the development of the M08-SO,[23] SOGGA11,[4] and M11[5] functionals, we enforced two physical

constraints on exchange and the same two on correlation; in particular, we require them to go to the correct UEG limit and to have the correct SO term in the density gradient expansion (that is, the correct coefficient of s^2). These UEG constraints translate to

$$a_0^{\mathbf{x}} + b_0^{\mathbf{x}} = 1 \tag{19}$$

$$a_0^{c} = 1 \tag{20}$$

while (as in eqs 30 to 32 in ref 23), the SO constraints yield

$$a_0^{\mathbf{x}}\mu^{\text{PBE}} + b_0^{\mathbf{x}}\mu_2 - \frac{5}{54}(a_1^{\mathbf{x}} + b_1^{\mathbf{x}}) = \mu_2 \tag{21}$$

$$a_1^{c} = 0, \ b_0^{c} = 1 \tag{22}$$

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

As in our recent M11 functional, 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. These constraints introduced in the B99 functional[32] were enforced in the τHCTH[33] and BMK[34] functionals and are enforced on the coefficients of the M11 and M11-L functional by

$$f_1(w = -1) + f_2(w = -1)$$
$$= \sum_{i'=0}^{m/2}(a_{2i'}^{\mathbf{x}} - a_{2i'+1}^{\mathbf{x}} + b_{2i'}^{\mathbf{x}} - b_{2i'+1}^{\mathbf{x}}) = 1 \tag{23}$$

$$f_1(w = 1) + f_2(w = 1) = \sum_{i=0}^{m}(a_i^{\mathbf{x}} + b_i^{\mathbf{x}}) = 1 \tag{24}$$

All constraints are imposed on both the short-range and the long-range parts of the two exchange terms to ensure that the entire functional respects the constraints. We also required that both kinetic-energy-density enhancement factors are everywhere positive.

Optimization. The optimization of M11-L is performed by minimizing a training function given by

$$F = w_1 R(\text{SB1AE97}) + w_2 R(\text{SRMBE13})$$
$$+ w_3 R(\text{LB1AE12}) + w_4 R(\text{MRBE10})$$
$$+ w_5 R(\text{IsoL6/11}) + w_6 R(\text{IP13/03})$$
$$+ w_7 R(\text{EA13/03}) + w_8 R(\text{PA8/06})$$
$$+ w_9 R(\text{ABDE4/05}) + w_{10} R(\text{ABDEL8})$$
$$+ w_{11} R(\text{HC7/11}) + w_{12} R(\pi\text{TC13})$$
$$+ w_{13} R(\text{HTBH38/08})$$
$$+ w_{14} R(\text{NHTBH38/08})$$
$$+ w_{15} R(\text{NCCE31/05}) + w_{16} R(\text{DC10})$$
$$+ w_{17} R(\text{AE17}) + w_{18} R(\text{SSLC15}) \tag{25}$$

where w_n is a weight and $R(D)$ is the root mean squared error of database D. Weights are not used in the calculation of the

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Table 1. Optimized Parameters for the M11-L Functional

	SR-exchange	LR-exchange	correlation
a_0	8.121131×10^{-1}	-4.386615×10^{-1}	1.000000
a_1	1.738124×10	-1.214016×10^2	0.000000
a_2	1.154007	-1.393573×10^2	2.750880
a_3	6.869556×10	-2.046649	-1.562287×10
a_4	1.016864×10^2	2.804098×10	9.363381
a_5	-5.887467	-1.312258×10	2.141024×10
a_6	4.517409×10	-6.361819	-1.424975×10
a_7	-2.773149	-8.055758×10^{-1}	-1.134712×10
a_8	-2.617211×10	3.736551	1.022365×10
b_0	1.878869×10^{-1}	1.438662	1.000000
b_1	-1.653877×10	1.209465×10^2	-9.082060
b_2	6.755753×10^{-1}	1.328252×10^2	6.134682
b_3	-7.567572×10	1.296355×10	-1.333216×10
b_4	-1.040272×10^2	5.854866	-1.464115×10
b_5	1.831853×10	-3.378162	1.713143×10
b_6	-5.573352×10	-4.423393×10	2.480738
b_7	-3.520210	6.844475	-1.007036×10
b_8	3.724276×10	1.949541×10	-1.117521×10^{-1}
ω^a	0.25		

[a]The value of ω is reported in bohr^{-1}.

final performance of the functional or the functionals to which it is compared; the weights are just a part of the subjective training process that is used to get good across-the-board performance for the various subdatabases. The weights that we used are those that provide performances comparable to or better than M06-L (which was by far the best previous local functional for BC338) for each subdatabase. During the optimization of the new functional, we found that obtaining good performance for SSLC15 usually corresponds to worsening the performances for the thermochemistry and noncovalent interactions databases. Therefore the weight for SSLC15 was chosen to obtain reasonable accuracy for lattice constants while keeping good performance for all other databases. The weights used in the training function for the optimization of M11-L are reported in the Supporting Information.

As for previous functionals, we first used post-SCF calculations to study the convergence of the results and the global behavior of the functional as functions of the weights and the number of terms in the expansion series of the enhancement factors (eqs 12−15, 17, and 18). We found that good convergence is achieved at $m = 8$, leading to a total of 54 parameters. The number of free parameters is reduced by the physical constraints that we enforce, bringing the total to 48, which is 10 more than M11 (because of the long-range DFT exchange), but only one more than the very successful M08-HX functional.

After the preliminary analysis, the 48 free coefficients of M11-L were optimized self-consistently at fixed values of ω, between 0 and 0.5 bohr^{-1}. We found that the value of the training function remains reasonably constant between $0.15 \leq \omega \leq 0.40$ bohr^{-1}, although the optimized coefficients for the short-range and the long-range parts change sensibly to compensate the changes in the ranges. We chose $\omega = 0.25$ bohr^{-1} as the final value, the same as used in the M11 functional.

The final values for all parameters in M11-L are in Table 1. The meta-GGA exchange enhancement factors for $s = 0$ are plotted as functions of w for both short-range and long-range in
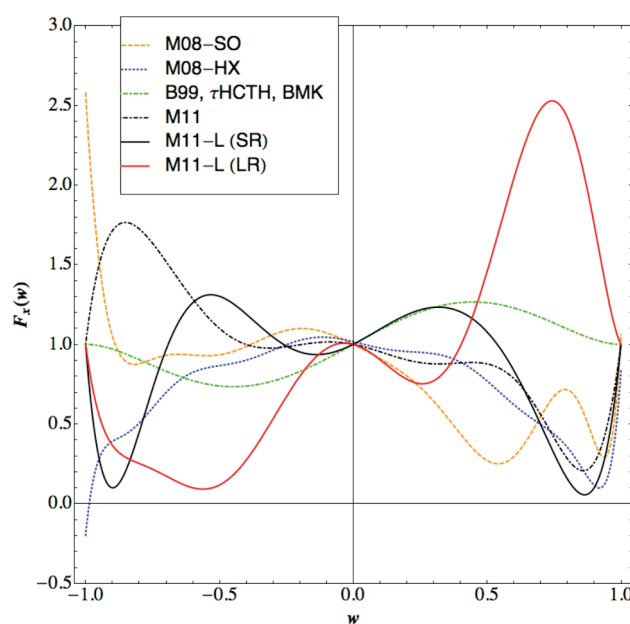

Figure 1. Exchange enhancement factors at $s = 0$ for the SR and LR terms of M11-L, compared to those of other meta-GGA functionals.

Figure 1, where they are compared to those of some other meta-GGA functionals. In the plots, 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. We see a radically different behavior for the short-range and long-range parts, which confirms that different regions of the interactions need different functional forms.

Implementation. The new functional has been defined such that the range separation is at the local level only. Thus the implementation of M11-L does not involve modifications to exchange integrals, and so it is much easier than that of range-separated hybrids. It is only slightly more complicated than that of single-range meta-GGAs, because it requires the calculation of the additional factor of eq 9. This extra term contains an

Table 2. MUEs (kcal/mol) for the BC338 Database and Its Subsets

	PBE	SOGGA11	B3LYP	B98	B97-3	SOGGA11-X	ωB97X	ωB97X-D	M05	M05-2X	M06-L	M06	M06-2X	M06-HF	M08-HX	M08-SO	M11	M11-L
# parameters	0	18	3	16	19	19	14	15	22	22	38	38	38	38	44	44	40	49
% HF exchange	0	0	20	21.98	26.93	35.42	15.77–100	22.2–100	28	56	0	27	54	100	52.23	56.79	42.8–100	0
ω (a_0^{-1})							0.3	0.2									0.25	0.25
SB1AE97[a]	2.77	1.47	0.96	0.66	0.62	0.65	0.45	0.47	0.50	0.47	0.83	0.59	0.42	0.58	0.66	0.60	0.45	0.68
SRMBE13	3.87	9.09	2.88	2.64	3.59	3.28	3.98	2.76	3.09	3.86	3.41	2.77	3.90	6.98	3.36	2.87	4.55	3.21
LB1AE12[a]	12.96	8.39	2.14	2.22	1.96	3.27	2.43	2.25	2.91	2.91	2.25	2.28	2.18	5.67	2.43	2.36	2.58	2.94
MRBE10	19.73	7.12	22.47	21.99	25.85	30.76	25.61	26.02	16.38	42.30	10.64	18.60	44.93	75.50	50.87	47.70	43.54	6.14
IsoL6/11	1.98	1.73	2.61	1.93	2.07	1.85	1.55	1.15	2.75	1.22	2.76	1.27	1.53	2.46	0.59	1.19	1.10	1.57
IP13/03	3.62	4.74	4.76	3.23	3.54	3.20	2.82	3.02	2.82	3.55	3.08	3.28	2.56	3.80	3.42	3.58	3.64	3.11
EA13/03	2.27	5.23	2.33	1.90	2.13	1.55	2.01	1.86	2.97	2.04	3.83	1.85	2.14	3.31	1.32	2.72	0.89	5.54
PA8/06	1.34	2.11	1.02	1.53	2.54	1.85	1.51	2.36	2.26	1.34	1.88	1.84	1.65	2.28	1.08	1.64	1.03	2.17
ABDE4/05	4.09	5.00	8.73	4.99	4.74	4.68	3.70	3.73	5.98	2.45	5.54	2.84	2.12	4.43	2.67	2.51	2.45	5.14
ABDEL8	7.16	7.89	10.40	7.71	7.70	5.12	4.82	4.92	8.78	2.73	8.85	4.72	2.69	4.56	2.87	3.88	3.48	6.98
HC7/11	3.97	6.26	16.80	8.46	7.58	7.27	6.77	4.63	7.71	3.64	3.35	2.78	2.15	2.29	4.89	4.60	3.74	2.42
πTC13	6.01	7.61	6.06	7.01	7.10	5.78	3.94	5.82	5.18	3.05	6.52	4.08	1.51	1.92	1.98	1.87	2.12	5.47
HTBH38/08	9.31	6.57	4.23	4.16	2.28	1.79	2.01	2.36	1.94	1.28	4.15	1.98	1.14	2.07	0.72	1.07	1.30	1.44
NHTBH38/08	8.42	4.32	4.55	3.31	1.38	1.16	2.89	3.74	2.07	1.81	3.81	2.33	1.22	2.53	1.22	1.23	1.28	2.86
NCCE31/05	1.24	1.28	0.96	0.70	0.98	0.63	0.50	0.32	0.49	0.28	0.58	0.41	0.29	0.41	0.35	0.37	0.26	0.56
DC10	39.22	30.71	20.66	15.34	18.67	15.79	9.92	10.39	16.15	10.73	19.76	9.45	10.46	15.63	9.60	10.87	8.03	10.38
AE17	54.44	6.99	13.62	9.25	9.24	5.26	3.06	3.23	9.17	6.38	3.86	6.85	6.18	4.28	6.54	10.54	5.15	6.42
BC338[b]	8.82	5.01	4.77	3.80	3.65	3.27	2.87	3.02	3.25	3.21	3.45	2.69	3.03	4.75	3.27	3.51	2.98	2.67
BC328xMR[b]	8.24	4.80	4.11	3.15	2.89	2.36	2.11	2.25	2.76	1.95	3.13	2.13	1.70	2.52	1.76	2.10	1.70	2.49
BC321xAE[b]	6.40	4.91	4.30	3.51	3.35	3.16	2.86	3.01	2.93	3.04	3.42	2.47	2.86	4.78	3.10	3.14	2.87	2.47

[a]Errors for SB1AE97 and LB1AE12 are reported on a per bond basis by dividing the per molecule results by the average number of bonds per molecule (5.10 and 1.33, respectively), so they are effectively MUEs in bond dissociation energies. [b]The overall MUEs are calculated by using eq S3 of the Supporting Information.

exponential and an error function, but nevertheless the computational cost of the M11-L functional is not significantly larger than that of other meta-GGA local functionals.

FORTRAN routines for the M11-L functional are included in the Supporting Information and are also freely available in the Minnesota Functional Module on our webpage.[35]

Performance. We analyze the performance of the new functional on several databases representative of classes of chemical and physical properties. We compare the performances of the M11-L functional with those of the following GGA and meta-GGA approximations: PBE[29] and SOGGA11[4] (GGA functionals), B3LYP,[36−39] B98,[40] B97-3[41] and SOGGA11-X[7] (global hybrid GGAs), ωB97X[28] and ωB97X-D[42] (range-separated hybrid GGAs), and all previous Minnesota meta-GGA functionals: M05,[12] M05-2X,[13] M06-L,[6] M06,[21] M06-2X,[21] M06-HF,[43] M08-SO,[23] M08-HX[23] and M11[5] (among them, M06-L is local, M11 is a range-separated hybrid, and all others are global hybrids). Table 2 compares the overall energetic performance of each functional in terms of the MUE for the BC338 energetic database and its subdatabases and subsets. According to the MUE for BC338, and also for BC321xAE, M11-L is the best functional. The majority of the other considered functionals, even hybrid functionals, have an MUE of 0.4−6.2 kcal/mol (15−230%) higher than that of M11-L. M11-L has performances very similar to those of M06, which contains 27% of HF exchange. M11-L is very competitive even for the BC328xMR database, for which hybrid GGA and hybrid meta-GGA functionals are the top performers. For example, M11-L is better for BC328xMR than the M05 and M06-HF functionals, and only slightly worse than the SOGGA11-X and ωB97X-D functionals (all of these include some portion of HF exchange), and it does much better than any other local functional or hybrid GGA, including the popular B3LYP functional.

The performances of M11-L for the barrier heights sets (HTBH38/08 and NHTBH38/08) are extremely encouraging. M11-L is in fact the first local functional to provide errors for barrier heights, on average, well below 4 kcal/mol (average MUE for the two subsets is 2.15 kcal/mol). These results outperform by far those of M06-L, which was exceptional among local functionals, in having an average MUE for the two subsets of 3.98 kcal/mol.

Results for the SSLC15 database are collected in Table 3, where they are compared to those of other local functionals. Calculations for solid-state databases are practical at reasonable cost only for functionals without HF exchange, and therefore we compare the performances of M11-L to those of other

successful local functionals. M06-L was recently applied with reasonable success to solid-state physics calculations,[44−47] but its performance for lattice constants is not as good as that of less broadly accurate functionals, such as LSDA, PBE, or TPSS,[48] or of specialized functionals, such as PBEsol[50] and SOGGA.[44] A generalization is that functionals that are most accurate for chemical calculations are not the best functionals for solid-state lattice constants, and vice versa. M11-L goes some way toward remedying this because it is a local functional capable of top-level performance for chemical systems and, at the same time, is on average better than all the other considered local functionals, with the exception of the specialized functionals SOGGA and PBEsol and the relatively new revTPSS,[49] which was specifically proposed for accurate lattice constants and surface energies.

Meta-GGA hybrid functionals can achieve high accuracy for single-reference systems, but their HF exchange leads to poor performance for multireference systems. Functionals with no HF exchange are much more successful for the treatment of problems with quasidegenerate electronic configurations, for example for the set of 10 multireference bond energies considered in this letter, M06-L performs on average 75% better than high-HF-exchange Minnesota hybrid meta-GGA functionals (M05-2X, M06-2X, M08-HX, and M11), and about 40% better than small-HF-exchange Minnesota hybrid meta-GGA functionals (M05 and M06). Similarly, SOGGA11 provides results close to M06-L for the same multireference database, on average 60% better than SOGGA11-X. We find that M11-L is the very best functional for the MRBE10 subdatabase, with an MUE 14% smaller than SOGGA11's, 30% below M06-L's, and a factor of 3.7 better than B3LYP.

M11-L was constructed using a well behaved functional form. Neverhtheless, we recommend that one should usually use at least an ultrafine integration grid[51] to avoid integration errors.

Concluding Remarks. We presented a new local meta-GGA functional, called M11-L, that is correct to second order in both exchange and correlation and that involves an optimized dual-range exchange functional. M11-L is the first functional that includes a solid-state lattice constant database in the optimization procedure. The performance of M11-L is compared to those of several other functionals, including all the other Minnesota meta-GGA and hybrid meta-GGA functionals. M11-L has the best average performance for a set of 338 chemical data, and even has competitive performances also for a subset of 328 data that do not include the multireference database. Despite being not as accurate as specialized functionals, M11-L is also quite reasonable for solid-state lattice constants; thus it is an important step in filling the

Table 3. Mean Errors (in Å) for the SSLC15 Database and Its Subsets[a]

	main group (3)	semiconductor (4)	ionic (5)	transition metals (3)	SSLC15	BC338
SOGGA	0.026	0.017	0.024	0.019	0.021	24.22
PBEsol	0.023	0.030	0.027	0.019	0.025	22.24
revTPSS[b]	0.014	0.022	0.065	0.018	0.034	
TPSS	0.053	0.062	0.068	0.027	0.054	5.19
LSDA	0.090	0.013	0.084	0.040	0.056	38.82
PBE	0.034	0.079	0.085	0.064	0.067	8.53
M06-L	0.142	0.049	0.050	0.056	0.071	3.40
M11-L	0.043	0.029	0.054	0.077	0.050	2.60

[a]The number of solids in each subset is in parentheses. For perspective, the last column gives the MUE (in kcal/mol) for BC338. [b]Errors for revTPSS are taken from ref 49 and are not available for BC338.

gap between functionals best for chemistry and those best for solid-state physics.

ASSOCIATED CONTENT

ⓢ Supporting Information

Subdatabases of BC338, details of the calculation and results, extension to open shells (spin-polarized systems), and Fortran routines for the M11-L functional. This material is available free of charge via the Internet at http://pubs.acs.org.

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