

Cite this: *Phys. Chem. Chem. Phys.*, 2012, **14**, 13171–13174

www.rsc.org/pccp

An improved and broadly accurate local approximation to the exchange–correlation density functional: The MN12-L functional for electronic structure calculations in chemistry and physics†

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Received 18th June 2012, Accepted 2nd August 2012

DOI: 10.1039/c2cp42025b

We report a new local exchange–correlation energy functional that has significantly improved across-the-board performance, including main-group and transition metal chemistry and solid-state physics, especially atomization energies, ionization potentials, barrier heights, noncovalent interactions, isomerization energies of large molecules, and solid-state lattice constants and cohesive energies.

Kohn–Sham density functional theory has been very successful because of its high accuracy and affordable cost for systems too complex or large to be treated with reliable wave function methods.¹ The accuracy depends on the quality of the exchange–correlation (xc) functional, and low cost for extended systems (liquids, solids, and very large molecules) is most readily achieved by restricting the functional form of the xc functional to be local, *i.e.*, the xc energy density at a point is required to be a function of only local variables, usually the spin densities ρ_σ ($\sigma = \alpha, \beta$), their reduced gradients²

$$x_\sigma = |\nabla\rho_\sigma|/\rho_\sigma^{4/3}, \quad (1)$$

and the variables³

$$\tilde{\tau}_\sigma = \sum_{i=1}^{n_\sigma} |\nabla\psi_{i\sigma}|^2, \quad (2)$$

which are proportional to spin kinetic energy densities (n_σ is the number of occupied Kohn–Sham orbitals $\psi_{i\sigma}$). Note that locality excludes so called hybrid functionals that also depend on nonlocal Hartree–Fock exchange—such functionals can lead to even higher accuracy,¹ but our focus here is exclusively on the computationally more efficient local functionals.

It is practically and fundamentally important to learn how accurate an xc functional can be when built from a restricted set of ingredients. For a long time, no functional built solely from ρ_σ and x_σ was accurate for solid-state lattice constants and molecular atomization energies or for solid-state lattice constants and solid-state cohesive energies, but we showed

that by using a new kind of nonseparable (N) term, we can obtain a functional with simultaneous good accuracy for all three; the new functional is called N12.⁴ Here we add $\tilde{\tau}_\sigma$ to N12 to obtain an even more accurate functional called MN12-L.

Functional form

The motivation for the functional forms is the same as described elsewhere for N12,⁴ where arguments were presented in terms of the exponential falloff of the electron density as the distance from the nuclei is increased and the reinterpretation of the well established range separation formalism as a way to allow the gradient enhancement to depend on electron density. In the present communication, we generalize the N12 polynomial in two variables,

$$v_{x\sigma} = \frac{\omega_{x\sigma}\rho_\sigma^{1/3}}{1 + \omega_{x\sigma}\rho_\sigma^{1/3}}; \quad u_{x\sigma} = \frac{\gamma_{x\sigma}x_\sigma^2}{1 + \gamma_{x\sigma}x_\sigma^2}, \quad (3)$$

to also include a third variable,

$$w_\sigma = \frac{y_\sigma - 1}{y_\sigma + 1}; \quad (4)$$

where

$$y_\sigma = (3/5)(6\pi^2)^{2/3}\rho_\sigma^{5/3}/\tilde{\tau}_\sigma. \quad (5)$$

Then MN12-L becomes

$$E = E_{\text{nxc}} + E_c \quad (6)$$

where the nonseparable part is

$$E_{\text{nxc}} = \sum_\sigma \int \text{d}\mathbf{r} \left\{ \epsilon_{x\sigma}^{\text{UEG}} \sum_{i=0}^3 \sum_{j=0}^{3-i} \sum_{k=0}^{5-i-j} a_{ijk} v_{x\sigma}^i u_{x\sigma}^j w_\sigma^k \right\}, \quad (7)$$

which contains the usual Gáspár–Kohn–Sham (GKS)^{5,6} formula for the exchange energy of a uniform electron gas; and the additional dynamical correlation term E_c has the same form as in M08-HX,⁷ M08-SO,⁷ M11-L,⁸ and M11.⁹ The upper limits on the sums in eqn (2) achieve nearly optimum accuracy while keeping the total number of fitted parameters at a quite manageable 40. The incorporation of kinetic energy density is justified by arguments made previously,¹⁰ namely that kinetic energy density allows one to distinguish regions of space described by a single orbital (including one-electron regions)

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† Electronic supplementary information (ESI) available: Details of the databases used in the communication; results for subsets of the databases. See DOI: 10.1039/c2cp42025b

from many-orbital and many-electron regions, and also it allows us to distinguish regions of decaying density from bonding regions. The objective is to make the exchange energy density more realistic, so that when the large exchange interactions are modeled more realistically, the smaller correlation energy can be optimized in a physical way to improve medium-range and short-range correlation energy rather than restraining it unphysically it to compensate large systematic errors in the exchange.

Optimization of the functional

We optimized the coefficients of the MN12-L functional on a training set composed of databases for chemistry and solid-state physics. The training set for MN12-L is the same as that used for N12 except that the ionization potential (IP) database is expanded to include eight IPs of metal atoms and one metal-containing molecule and is now called IP21. A summary of databases used in the optimization procedure and for analysing the performance of the functional is in Table 1 with details in the ESI.†

For the nonlinear coefficients of MN12-L we used the same values as in N12 ($\omega_{x\sigma} = 2.5$ and $\gamma_{x\sigma} = 0.004$), while the linear coefficients, a_{ijk} , were optimized self-consistently to minimize

$$F = \sum_{n=1}^{18} h_n R_n, \quad (8)$$

where h_n is a fixed weight, and R_n is the root mean squared error of database n except that we used the root mean squared error per bond for MGAE109/11 and DC9/12 (see Table 1 for the details). During optimization, we constrained the absolute values of all coefficients to be no larger than 25, which we

found to be large enough to provide flexibility to the functional form, but not so large as to cause problems in the convergence of the self-consistent-field iterations. Weights were chosen by comparing the performance of the new functional to those of M11-L, so that MN12-L matches the good performance of M11-L for the chemistry databases and simultaneously provides good performance for the solid-state training databases. The weights are in Table 1, and the optimized coefficients are in Table 2.

All calculations in this communication were performed with a locally modified version^{11a} of the *Gaussian 09* program,^{11b} using the ultrafine (“99590”) Lebedev grid and allowing symmetry breaking of the wave function in order to converge to the stable broken-symmetry solution when this is the variationally best collinear solution to the Kohn–Sham equations (through the `STABLE = OPT Gaussian` keyword).

Performance

We assess the performance of the MN12-L functional on a set of databases that includes all 18 databases in the training set and four databases that are not included in the training set. Since MN12-L is optimized to be competitive for both chemistry and solid-state physics and to be applicable to the largest target systems, we focus mainly on local functionals; in particular we compare to five functionals that depend only on the density and its gradient (SOGGA,¹² SOGGA11,¹³ N12,⁴ PBE,¹⁴ and PBEsol¹⁵) and four local meta-GGA functionals (TPSS,¹⁶ revTPSS,¹⁷ M06-L¹⁸ and M11-L⁸). We also include one screened-exchange hybrid GGA (HSE^{19,20}), which is more practical than global hybrids for solid-state

Table 1 Summary of the databases used in the current work

n	Database ^a	Description	Weight ^b	Ref.
<i>Energetic set</i>				
1	MGAE109/11 ^c	Main group atomization energies	150	24, 25
2	SRMBE13	Single-reference metal bond energies	10	8
3	MRBE10	Multi-reference bond energies ^d	10	8
4	IsoL6/11	Isomerization energies of large molecules	2	26
5	IP21	Ionization potentials	16	10b, 24, 27, 28 and present
6	EA13/03	Electron affinities	1	10b, 24, 27, 28
7	PA8/06	Proton affinities	4	29
8	ABDE4/05	Alkyl bond dissociation energies	4	18, 24, 30
9	ABDEL8	Alkyl bond dissociation energies of large molecules	3	13, 30
10	HC7/11	Hydrocarbons	4	13
11	π TC13	Thermochemistry of π systems	15	18, 27, 29
12	HTBH38/08	Hydrogen transfer barrier heights	50	24, 31, 32
13	NHTBH38/08	Non-hydrogen transfer barrier heights	50	24, 31, 32
14	NCCE31/05	Non-covalent complexation energies	200	10b, 33
15	DC9/12 ^c	Difficult cases	4	4
16	AE17	Atomic energies	1	34, 35
<i>Structural set</i>				
17	SSLC18	Solid-state lattice constants	40	8, 12
18	DG6	Geometries of diatomic molecules	40	4
<i>Test set</i>				
19	SLC34	Semiconductors lattice constants	0	36
20	SBG31	Semiconductors band gaps	0	36
21	SSCE8	Solid-state cohesive energies	0	12
22	MGBL20	Main group bond lengths	0	12

^a Details of the geometries, reference data, and basis sets used for the various databases are available in the ESI. ^b Weights (h_1 to h_{16} in [cal mol⁻¹], h_{17} and h_{18} in Å⁻¹) used in the training function (eqn (8)). ^c The errors of the MGAE109/11 and DC9/12 subdatabases are reported on a per bond basis, by dividing the per molecule average errors by the average number of bonds broken or rearranged in the database (4.71 for MGAE109/11, 9.22 for DC9/12). ^d Five involving transition metal bonds and five non-metal cases.

Table 2 Optimized parameters for the MN12-L functional

Exchange		Correlation			
a_{000}	6.73598×10^{-1}	a_{102}	4.40745	b_0	8.84461×10^{-1}
a_{001}	-2.27060	a_{103}	-2.00819×10	b_1	-2.20228×10^{-1}
a_{002}	-2.61371	a_{104}	-1.25356×10	b_2	5.70137
a_{003}	3.99361	a_{110}	-5.43503	b_3	-2.56238
a_{004}	4.63557	a_{111}	1.65674×10	b_4	-9.64683×10^{-1}
a_{005}	1.25068	a_{112}	2.00023×10	b_5	1.98218×10^{-1}
a_{010}	8.44492×10^{-1}	a_{113}	-2.51311	b_6	1.01998×10
a_{011}	-1.30117×10	a_{120}	9.65844	b_7	9.78935×10^{-1}
a_{012}	-1.77773×10	a_{121}	-3.82528	b_8	-1.51272
a_{013}	-4.62721	a_{122}	-2.50000×10	c_0	5.32395×10^{-1}
a_{014}	5.97660	a_{200}	-2.07008	c_1	-5.83191
a_{020}	1.14290	a_{201}	-9.95191	c_2	3.88239
a_{021}	-2.04023×10	a_{202}	8.73121×10^{-1}	c_3	5.87849
a_{022}	-2.38284×10	a_{203}	2.21089 $\times 10$	c_4	1.49323×10
a_{023}	7.11911	a_{210}	8.82263	c_5	-1.37464×10
a_{030}	-2.33573×10	a_{211}	2.49995 $\times 10$	c_6	-8.49233
a_{031}	-1.62263×10	a_{212}	2.50000 $\times 10$	c_7	-2.48655
a_{032}	1.48273 $\times 10$	a_{300}	6.85169×10^{-1}	c_8	-1.82235×10
a_{100}	1.44928	a_{301}	-7.40695×10^{-2}		
a_{101}	1.02060×10	a_{302}	-6.78800×10^{-1}		

calculations because it does not include the computationally expensive nonlocal Hartree–Fock exchange at large interelectronic separations. MN12-L results for the chemical databases are reported in terms of mean unsigned errors (MUEs) and compared to those of the other functionals in Table 3.

Considering the 16 chemical databases individually, MN12-L is the top performer for six of them, in particular main group atomization energies, isomerization energies of large molecules, ionization potentials, both sets of barrier heights, and non-covalent interactions; for the other ten, MN12-L is very close to the top performer. In terms of the overall MUE for the

entire chemistry energetic set (dubbed BC345 for broad chemistry database with 345 data), MN12-L is by far the best functional, beating the previous best (M11-L) by more than 30%. Since errors for atomic energies will sometimes be cancelled out for chemical processes, we also considered another average (called (BC328xAE) by excluding AE17; again MN12-L is the best performer, beating the previous best functional (once again M11-L) by about 15%.

MN12-L is better than M06-L for all databases except three (SRMBE13, PA8/06, and AE17), while it is better than M11-L in all databases except five (SRMBE13, MRBE10, HC7/11, π TC13, and DC9/12); however in all these cases MN12-L is very close to the performance of the previous functional, while for the other databases and for the overall averages it performs much better.

As compared to the nonlocal HSE screened-exchange hybrid, MN12-L performs better in all chemistry databases except two (SRMBE13 and PA8/08, note that for these two databases the more expensive HSE is the top performer among the considered functionals); the overall MUE for BC345 for MN12-L is 2.4 kcal mol⁻¹ better than that of HSE, which is a quite encouraging result for a functional without Hartree–Fock exchange.

Local functionals are often preferred to nonlocal ones for transition metal (TM) chemistry because Hartree–Fock exchange introduces excessive ionicity and localization for weakly overlapping orbitals on different centers.^{21,22} The MUEs for the primary subdatabases in Table 3 do not explicitly illustrate the accuracy for TM chemistry, but in the TMBE15 row, we extracted all 15 TM bond energies—10 from SRMBE13 and 5 from MRBE10. Table 3 shows that MN12-L is better for TM bond energies than any xc functional except M11-L, and it outperforms many of the competitors by a large margin.

Table 3 MUEs (kcal mol⁻¹) for the chemistry energetic databases (among each type, functionals are ordered according to the year in which they were first proposed)

Type	GGA	GGA	GGA	GGA	NGA	hybrid-GGA	meta-GGA	meta-GGA	meta-GGA	meta-GGA	meta-GGA	meta-GGA
Functional	PBE	SOGGA	PBEsol	SOGGA11	N12	HSE	TPSS	revTPSS	M06-L	M11-L	MN12-L	meta-NGA
<i>Primary subsets</i>												
MGAE109/11 ^b	3.07	7.82	7.94	1.68	1.27	0.88	1.07	0.94	0.87	0.74	0.69	
SRMBE13	3.61	5.44	5.46	6.26	4.56	2.35	2.91	3.28	3.40	3.21	3.95	
MRBE10	19.27	23.99	27.12	14.30	6.65	25.09	10.60	11.35	9.97	6.14	7.12	
IsoL6/11	1.98	1.89	1.55	1.73	1.73	1.25	3.66	3.96	2.76	1.57	1.07	
IP21	6.27	4.75	5.82	6.29	6.84	4.07	4.20	3.98	3.82	4.58	3.54	
EA13/03	2.27	2.70	2.16	5.23	3.89	2.77	2.35	2.59	3.83	5.54	2.42	
PA8/06	1.34	2.33	2.10	2.11	1.35	1.10	2.66	2.79	1.88	2.17	1.91	
ABDE4/05	4.09	5.09	4.03	5.00	3.81	5.82	9.56	7.64	5.54	5.14	4.25	
ABDEL8	7.16	3.87	3.18	7.89	6.54	8.70	10.93	9.02	8.85	6.98	5.16	
HC7/11	3.97	17.88	13.31	6.26	4.27	7.34	10.48	6.42	3.35	2.42	2.58	
π TC13	6.01	4.72	4.84	7.61	8.69	6.17	8.16	7.93	6.52	5.47	5.61	
HTBH38/08	9.31	12.88	12.69	6.57	6.94	4.23	7.71	6.96	4.15	1.44	1.31	
NHTBH38/08	8.42	9.68	9.86	4.32	6.86	3.73	8.91	9.07	3.81	2.86	2.24	
NCCE31/05	1.24	1.84	1.79	1.28	1.30	0.75	1.17	1.14	0.58	0.56	0.46	
DC9/12 ^b	4.27	9.24	8.93	3.33	3.02	1.96	1.95	2.28	2.36	1.14	1.65	
AE17	47.24	283.06	245.9	10.06	14.21	32.82	18.04	23.81	7.04	21.81	9.73	
<i>Transition metals^a</i>												
TMBE15	9.62	14.96	14.53	11.67	5.47	14.99	7.58	8.06	7.74	4.43	5.26	
<i>Averages</i>												
BC345	7.22	21.38	19.58	4.39	4.13	4.76	4.98	5.05	3.08	3.20	2.33	
BC328xAE	5.15	7.81	7.85	4.10	3.91	3.30	4.31	4.08	2.88	2.24	1.95	

^a The first 16 rows of this table are nonoverlapping subsets of the BC345 database, but the next row contains a subset of this data regrouped to assess the accuracy of the xc functionals for transition metal chemistry. ^b The errors of the MGAE109/11 and DC9/12 subdatabases are reported on a per bond basis, by dividing the per molecule average errors by the average number of bonds broken or rearranged in the database (4.71 for MGAE109/11, 9.22 for DC9/12).

Table 4 MUEs for the structural databases in the training set and for the four databases used only for testing (lattice constants and bond lengths are in Å, band gaps in eV, and cohesive energies in eV per atom)

Functional	Type	SSLC18	DG6	SLC34	SBG31	SSCE8	MGBL20
PBE	GGA	0.067	0.013	0.097	0.98	0.11	0.010
SOGGA	GGA	0.021	0.009	0.027	1.14	0.27	0.010
PBEsol	GGA	0.025	0.010	0.035	1.14	0.31	0.010
SOGGA11	GGA	0.122	0.008	0.104	0.89	0.07	0.006
N12	NGA	0.021	0.008	0.035	0.99	0.13	0.008
HSE	hybrid-GGA	0.035	0.003	0.051	0.26	0.11	0.006
TPSS	meta-GGA	0.054	0.011	0.083	0.85	0.22	0.007
revTPSS	meta-GGA	0.034	0.011	0.061	1.00	0.13	0.008
M06-L	meta-GGA	0.071	0.006	0.088	0.73	0.17	0.004
M11-L	meta-GGA	0.050	0.011	0.071	0.54	0.24	0.010
MN12-L	meta-NGA	0.019	0.005	0.039	0.84	0.11	0.008

Results for the two structural databases included in the training set are reported in the first two numerical columns of Table 4, while those for the four databases in the additional test set are reported in the last four columns. The band gaps in the SBG31 column are approximated as crystal orbital HOMO–LUMO gaps, but they should not be overinterpreted because this approximation is not accurate even with the exact Kohn–Sham potential.²³ MN12-L performs slightly better than TPSS, revTPSS, and functionals without $\bar{\tau}_{\sigma}$, but worse than HSE, M06-L, and M11-L for band gaps.

MN12-L is the top performer for the two structural databases in the training set (SSLC18 and DG6), with MUEs better than that of PBEsol, which is a specialized functional designed for the solid state, and substantially better than PBE, TPSS, M06-L, and M11-L. MN12-L delivers results that are on a par with PBEsol for both the semiconductor lattice constants and the diverse molecular bond length databases and much better for solid-state cohesive energies, for which it also outperforms N12. SOGGA11 is the best performer for SSCE8, but its performances for the structural solid-state databases are disappointing.

Table 4 shows that the performance of MN12-L for all four databases not used in training is quite satisfactory.

Conclusions

MN12-L maintains the high performance of M11-L for all chemistry databases considered, being better for 11 of the 16 and is much improved on the solid-state databases—for example, it has an average performance for lattice constants comparable to that of the specialized PBEsol functional. MN12-L has the best across-the-broad performance of any local functional and is equally well suited for chemistry and physics and for energies and structures.

Acknowledgements

This work was supported in part by the by the Air Force Office of Scientific Research by grant FA9550-11-0078 and the National Science Foundation by grant CHE09-56776.

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