PCCP
Dynamic Article Links

Cite this: *Phys. Chem. Chem. Phys.*, 2012, **14**, 16187–16191

www.rsc.org/pccp

COMMUNICATION

Screened-exchange density functionals with broad accuracy for chemistry and solid-state physics†

Roberto Peverati and Donald G. Truhlar*

Received 27th July 2012, Accepted 17th September 2012
DOI: 10.1039/c2cp42576a

We present two new exchange–correlation functionals for hybrid Kohn–Sham electronic structure calculations based on the non-separable functional form introduced recently in the N12 and MN12-L functionals but now with the addition of screened Hartree–Fock exchange. The first functional depends on the density and the density gradient and is called N12-SX; the second functional depends on the density, the density gradient, and the kinetic energy density and is called MN12-SX. Both new functionals include a portion of the Hartree–Fock exchange at short-range, but Hartree–Fock exchange is screened at long range. The accuracies of the two new functionals are compared to those of the recent N12 and MN12-L local functionals to show the effect of adding screened exchange, are compared to the previously best available screened exchange functional, HSE06, and are compared to the best available global-hybrid generalized gradient approximation (GGA) and to a high-performance long-range-corrected meta-GGA.

Kohn–Sham density functional theory is exact in principle but is limited in practice by our ability to approximate the unknown exchange–correlation (xc) functional.[1] The functional form chosen for the xc functional is usually based on a combination of computational simplicity and physical considerations. Progress has largely consisted in designing new functional dependencies and determining the parameters by fundamental constraints, models (such as the uniform electron gas), and empirical data. Constraints and models are only sufficient for fitting a few parameters, so the most broadly accurate functionals are those that have been parameterized against broad sets of experiment data, improving on the pioneering parametrization strategy of Becke.[2,3] The success of such parameterizations depends on the quality and diversity of the fitted data and the flexibility and physicality of the functional form, and functionals restricted in form and fit to data or constraints of limited diversity cannot be expected to be accurate across broad categories of chemical and physical data. The inadequacy of limited functional forms is demonstrated by the lack of success in attempts to simultaneously fit solid-state lattice constants and molecular atomization energies with a three-parameter generalized gradient approximation.[4] This problem was overcome recently[5] by a nonseparable form motivated by the earlier successful introduction[6–10] of range separation. More generally, the progress in functional development has been punctuated by successive adoption of more and more flexible forms, for example, building in more general dependence on spin densities (ρ_σ), their gradients, Hartree–Fock exchange energy density, and kinetic energy density. When flexible functional forms containing the right physics are combined with diverse and well-balanced training sets, one can obtain xc functionals with broad applicability in chemistry and physics.[10,11]

It is now generally recognized that replacing a portion of local density functional exchange in an xc functional by nonlocal orbital-dependent Hartree–Fock (HF) exchange improves the energetic predictions on molecules,[12] but one pays three heavy costs. First is the loss of some left–right correlation, which is included naturally in local density-dependent exchange functionals.[13] Second is the increased computational cost of HF exchange,[14] especially for extended systems treated with plane wave basis sets.[15–17] Third is the possibility of overestimating spin polarization of atoms and therefore underestimating metallic cohesive energies.[18] The first problem generally leads to a compromise in which 5–60% HF exchange is included, rather than 0 or 100%. One way to ameliorate the second problem is the so called screened exchange (SX) version of range separation in which the electron exchange for small interelectronic distances is treated with a finite percentage of nonlocal HF exchange, but the nonlocality is screened at large distances, and electron exchange at long range is treated by a local approximation.[14,19] Screening the nonlocal exchange has been particularly successful for the calculation of band gaps of semiconductors.[14,19–25] Not only is it computationally advantageous, but it can be justified on the physical grounds that nonlocal exchange may be screened at long range by correlation effects.[26]

We have recently proposed two new xc functionals with very encouraging performance, N12[5] based on a nonseparable gradient approximation (NGA) and MN12-L[27] in which dependence on kinetic energy density is added to N12. In the present communication we improve both of these xc functionals by adding a dependence on screened HF exchange. The resulting functionals are called N12-SX and MN12-SX.

Department of Chemistry – University of Minnesoata, Minneapolis, Minnesota 55455, USA. E-mail: truhlar@umn.edu

† Electronic supplementary information (ESI) available: Details of the databases used in the communication; results for subsets of the databases. See DOI: 10.1039/c2cp42576a

Functional form

The new N12-SX and MN12-SX functionals have the form

$$E = (X/100)E_{\rm x}^{\rm SR\text{-}HF} + E_{\rm xc}^{\rm L\text{-}DFT} \quad (1)$$

where the first component is the nonlocal HF exchange calculated by using the short-range term of the range-separated Coulomb operator (where r is the interelectronic separation):

$$\frac{1}{r} = \underbrace{\frac{\mathrm{erfc}(\mu r)}{r}}_{\rm SR} + \underbrace{\frac{\mathrm{erf}(\mu r)}{r}}_{\rm LR}. \quad (2)$$

The second term in eqn (1) has a local form:

$$E_{\rm xc}^{\rm L\text{-}DFT} = E_{\rm nxc} + E_{\rm c} \quad (3)$$

where the nonseparable exchange-correlation part is:

$$E_{\rm nxc} = \sum_{\sigma} \int \mathrm{d}\mathbf{r} \left\{ \varepsilon_{{\rm x}\sigma}^{\rm UEG} \sum_{i=0}^{m} \sum_{j=0}^{m'} \sum_{k=0}^{m''} a_{ijk} v_{{\rm x}\sigma}^{i} u_{{\rm x}\sigma}^{j} w_{\sigma}^{k} \right\} \quad (4)$$

which contains the usual Gáspár–Kohn–Sham (GKS)[28,29] formula for the exchange energy of a uniform electron gas; and a nonseparable functional form that depends on transformations of the spin densities, their gradients and the kinetic energy densities into more convenient finite variables:

$$v_{{\rm x}\sigma} = \frac{\omega_{{\rm x}\sigma}\rho_{\sigma}^{1/3}}{1+\omega_{{\rm x}\sigma}\rho_{\sigma}^{1/3}} \in [0,1]; \quad u_{{\rm x}\sigma} = \frac{\gamma_{{\rm x}\sigma}x_{\sigma}^{2}}{1+\gamma_{{\rm x}\sigma}x_{\sigma}^{2}} \in [0,1];$$
$$w_{\sigma} = \frac{y_{\sigma}-1}{y_{\sigma}+1} \in [-1,1]. \quad (5)$$

where[30,31]

$$x_{\sigma} = |\nabla\rho_{\sigma}|/\rho_{\sigma}^{4/3}, \quad (6)$$

$$y_{\sigma} = (3/5)(6\pi^{2})^{2/3}\,\rho_{\sigma}^{5/3}/\tilde{\tau}_{\sigma}, \quad (7)$$

and

$$\tilde{\tau}_{\sigma} = \sum_{i=1}^{n_{\sigma}} |\nabla\psi_{i\sigma}|^{2} \quad (8)$$

where $\psi_{i\sigma}$ is an occupied Kohn–Sham orbital. Note that $E_{\rm nxc}$ includes correlation effects along with exchange in a nonseparable way, which, one can argue,[5] is general enough to stand in for explicit separation of ranges, as well as including other nonseparable effects.

In the N12-SX functional, we use a nonseparable part obtained from eqn (4) using:

$$m = 3, \quad m' = 3, \quad m'' = 0 \quad (9)$$

and we use the B97 GGA functional form[2] with truncation at the fourth power for the correlation, for a total of 26 parameters. In the MN12-SX functional the nonseparable part is obtained from eqn (4), using:

$$m = 3, \quad m' = 3 - i, \quad m'' = 5 - i - j \quad (10)$$

while we use the M08[32] and M11[33] meta-GGA functional form truncated at the eighth power for the correlation, for a total of 40 parameters.

Optimization of the functionals

We optimized the coefficients of the N12-SX and MN12-SX functionals on a training of 369 chemistry and physics data; this data is the same as that used for MN12-L[27] (and differs from that used for N12 only by the addition of eight ionization potentials); 345 of the data, grouped as the BC345 data set are broad chemistry energetic data, and 24 data are structural. A summary of databases used in the optimization procedure and for analysing the performance of the functional is in Table 1, which includes references[5,10,11,27,34–49] for the data; further details are in the ESI.†

For the nonlinear coefficients of the nonseparable term, we used the same values as in N12 and MN12-L ($\omega_{{\rm x}\sigma} = 2.5a_0$ and $\gamma_{{\rm x}\sigma} = 0.004$). A study of the influence of the value of the short-range percentage of Hartree–Fock exchange, X, and the range-defining parameter μ on the quality of the results and the computational cost for extended systems was performed by Krukau *et al.*,[19] and led to a revision of the HSE[14] functional that is sometimes called HSE06; we use the HSE06 values, *i.e.*, $X = 25$ and $\mu = 0.11{a_0}^{-1}$. The linear coefficients, a_{ijk}, were optimized self-consistently without constraints to minimize:

$$F = \sum_{n=1}^{18} h_n R_n, \quad (11)$$

where h_n is a fixed weight, and R_n is the root mean squared error of database n except that we used the mean squared error per bond for MGAE109/11 and DC9/12 (see Table 1 for the details). Weights were chosen for each functional form by comparing the performance of the new functional to those of SOGGA11-X in the case of N12-SX, and to those of M11 in the case of MN12-SX, so that the new functional can respectively match the good performance of these functional for the chemistry databases and simultaneously provide good performance for the solid-state training databases.

The weights used in both procedures are reported in the ESI,† while the optimized coefficients for N12-SX are in Table 2, and those for MN12-SX are in Table 3.

All calculations in this communication were performed with a locally modified version[50] of the *Gaussian 09* program,[51] using the ultrafine ("99 590") Lebedev grid and allowing symmetry breaking of atomic and molecular wave functions in order to converge to the stable broken-symmetry solution when this is the variationally best collinear solution to the Kohn–Sham equations (by using the stable optimization option of *Gaussian 09*). Calculations on the solid-state physics databases were carried out by the periodic boundary conditions (PBC) algorithm[52] of *Gaussian 09* using the same methodology as in our previous work,[47,53] which employs the m-6-311G* basis set.[21]

Performance

We assess the performance of the two new functionals 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. Analysis is carried out in terms of mean unsigned errors (MUEs), which are in all cases computed without using any

Table 1 Summary of the databases used in the current work

n	Database[a]	Description	Ref.
	Energetic set (BC345)		
1	MGAE109/11[b]	Main group atomization energies	34, 48
2	SRMBE13	Single-reference metal bond energies	10
3	MRBE10[c]	Multi-reference bond energies	10
4	IsoL6/11	Isomerization energies of large molecules	35
5	IP21	Ionization potentials	27, 34, 36–38, 49
6	EA13/03	Electron affinities	34, 36–38
7	PA8/06	Proton affinities	39
8	ABDE4/05	Alkyl bond dissociation energies	34, 40, 41
9	ABDEL8	Alkyl bond dissociation energies of large molecules	41, 42
10	HC7/11	Hydrocarbons	42
11	πTC13	Thermochemistry of π systems	37, 39, 43
12	HTBH38/08	Hydrogen transfers barrier heights	34, 43, 44
13	NHTBH38/08	Non-hydrogen transfers barrier heights	34, 43, 44
14	NCCE31/05	Non-covalent complexation energies	36, 45
15	DC9/12[b]	Difficult cases	5
16	AE17	Atomic energies	11, 46
	Structural set		
17	SSLC18	Solid state lattice constants	10, 52
18	DG6	Geometries of diatomic molecules	5
	Test set		
19	SLC34	Semiconductors lattice constants	47
20	SBG31	Semiconductors band gaps	47
21	SSCE8	Solid-state cohesive energies	52
22	MGBL20	Main group bond lengths	52

[a] Details of the geometries, reference data, and basis sets used for the various databases are available in the ESI. [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). [c] Five involving transition metal bonds and five being non-metal cases.

weights. Results for the chemical databases are in Table 4, where we compare the two new functionals to the previous nonseparable functionals, N12[5] and MN12-L,[27] as well as our recent SOGGA11-X global hybrid GGA,[48] M11 range-separated hybrid meta-GGA,[33] and HSE06[19] screened-exchange. We note that SOGGA11-X is particularly informative for comparison because if one excludes multireference bond energies (MRBE10), it is the best performing functional in the popular global-hybrid GGA class (even including MRBE10, its MUE for BC345 is 1.50 kcal mol^{-1} better than that of the popular B3LYP).

The overall performance of N12-SX is outstanding for a functional that does not include kinetic energy density. It is 1.15 kcal mol^{-1} better than N12, and it is very similar to SOGGA11-X (0.06 kcal mol^{-1} worse for BC345, but 0.21 kcal mol^{-1} better for BC328xAE), with the clear advantage of being at the same time more affordable, especially for extended systems. It has noteworthy good performance for transition metal bond energies and is relatively weakest for hydrocarbon thermochemistry.

MN12-SX is even better, 1.17 kcal mol^{-1} better than N12-SX, showing the power of including kinetic energy density. MN12-SX is also 1.24 kcal mol^{-1} better than M11, along with having the computational advantage of no long-range nonlocal exchange. MN12-SX is 0.45 kcal mol^{-1} better than MN12-L, showing the power of screened exchange. Especially noteworthy is the performance of MN12-SX for main-group

Table 2 Optimized parameters for the N12-SX functional

Exchange		Correlation	
a_{000}	0.681116	b_0	2.63373
a_{100}	1.88858	b_1	−1.05450
a_{200}	1.78590	b_2	−0.729853
a_{300}	0.879456	b_3	4.94024
a_{010}	−0.081227	b_4	−7.31760
a_{110}	−1.08723		
a_{210}	−4.18682	c_0	0.833615
a_{310}	−30.0000	c_1	3.24128
a_{020}	0.536236	c_2	−10.6407
a_{120}	−5.45678	c_3	−16.0471
a_{220}	30.0000	c_4	25.1047
a_{320}	55.1105		
a_{030}	−0.709913		
a_{130}	13.0001		
a_{230}	−72.4877		
a_{330}	29.8363		

Table 3 Optimized parameters for the MN12-SX functional

Exchange				Correlation	
a_{000}	0.5226556	a_{102}	11.07987	b_0	0.7171161
a_{001}	−0.2681208	a_{103}	−11.82087	b_1	−2.380914
a_{002}	−4.670705	a_{104}	−11.17768	b_2	5.793565
a_{003}	3.067320	a_{110}	−5.821000	b_3	−1.243624
a_{004}	4.095370	a_{111}	22.66545	b_4	13.64920
a_{005}	2.653023	a_{112}	8.246708	b_5	−21.10812
a_{010}	0.5165969	a_{113}	−4.778364	b_6	−15.98767
a_{011}	−20.35442	a_{120}	0.5329122	b_7	14.29208
a_{012}	−9.946472	a_{121}	−6.666755	b_8	6.149191
a_{013}	2.938637	a_{122}	1.671429		
a_{014}	11.31100	a_{200}	−3.311409	c_0	0.4663699
a_{020}	4.752452	a_{201}	0.3415913	c_1	−9.110685
a_{021}	−3.061331	a_{202}	−6.413076	c_2	8.705051
a_{022}	−25.23173	a_{203}	10.38584	c_3	−1.813949
a_{023}	17.10903	a_{210}	9.026277	c_4	−0.4147211
a_{030}	−23.57480	a_{211}	19.29689	c_5	−10.21527
a_{031}	−27.27754	a_{212}	26.69232	c_6	0.8240270
a_{032}	16.03291	a_{300}	1.517278	c_7	4.993815
a_{100}	1.842503	a_{301}	−3.442503	c_8	−25.63930
a_{101}	1.927120	a_{302}	1.100161		

Table 4 MUEs (kcal mol^{-1}) for the chemistry energetic databases (functionals are ordered according to the year in which they were first proposed)

Type[a] Functional	SX-GGA HSE06	GH-GGA SOGGA11-X	RSH-mGGA M11	NGA N12	mNGA MN12-L	SX-NGA N12-SX	SX-mNGA MN12-SX
MGAE109/11[b]	0.88	0.73	0.52	1.27	0.69	0.76	0.52
SRMBE13	2.35	3.36	4.04	4.56	3.95	3.22	4.03
MRBE10	25.09	37.18	43.83	6.65	7.12	8.47	10.49
IsoL6/11	1.25	1.85	1.10	1.73	1.07	1.78	1.21
IP21	4.01	3.69	7.21	3.48	3.48	4.06	5.11
EA13/03	2.77	1.55	0.89	3.89	2.65	2.73	1.62
PA8/06	1.10	1.85	1.03	1.35	1.91	1.97	1.16
ABDE4/05	5.82	4.68	2.45	3.81	4.25	3.73	3.42
ABDEL8	8.70	5.12	3.48	6.54	5.16	6.08	4.03
HC7/11	7.34	7.27	3.74	4.27	2.58	11.05	2.21
πTC13	6.17	5.78	2.12	8.69	5.61	7.64	3.57
HTBH38/08	4.23	1.79	1.30	6.94	1.31	3.71	0.95
NHTBH38/08	3.73	1.16	1.28	6.86	2.24	2.83	1.35
NCCE31/05	0.75	0.63	0.26	1.30	0.46	0.74	0.30
DC9/12[b]	1.96	1.66	0.80	3.02	1.65	1.19	1.20
AE17	32.82	4.98	8.88	14.21	9.73	10.22	4.52
BC345	4.75	3.00	3.13	4.21	2.34	3.06	1.89
BC328xAE	3.30	2.90	2.83	3.69	1.95	2.69	1.75

[a] SX = screened-exchange; GH = global hybrid; RSH = range-separated hybrid; an m as a prefix in the type row denotes meta. [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 5 MUEs for the structural databases in the training set and for the databases used only for testing (lattice constants and bond lengths are in Å, band gaps in eV, and cohesive energies in eV atom^{-1})

Functional	Type	SSLC18	DG6	SLC34	SBG31	SSCE8	MGBL20
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
HSE06	SE-GGA	0.035	0.003	0.051	0.26	0.11	0.006
N12	NGA	0.021	0.008	0.035	0.99	0.13	0.008
MN12-L	mNGA	0.019	0.005	0.039	0.84	0.11	0.008
N12-SX	SE-NGA	0.022	0.005	0.034	0.26	0.11	0.008
MN12-SX	SE-mNGA	0.025	0.003	0.044	0.32	0.15	0.007

atomization energies, hydrocarbon and π system thermochemistry, hydrogen-transfer barrier heights, and atomic energies.

The comparison of N12-SX results with those for the previous screened-exchange hybrid HSE06 shows that our careful parametrization provide a more balanced functional, which is on average 1.69 kcal mol^{-1} better than HSE06 at a similar computational cost. MN12-SX is 2.86 kcal mol^{-1} better than HSE06, with especially improved performance (a factor of 1.5 or better) for main-group atomization energies, multireference and alkyl bond energies, electron affinities, hydrocarbon and π system thermochemistry, both sets of barrier heights, noncovalent interaction energies, difficult cases, and atomic energies.

Considering the fact that hybrid functionals are not particularly well suited for treating multi-reference systems, the performance of both new functionals for the multi-reference database is also encouraging. In this respect we note that both N12-SX and MN12-SX have a maximum percentage of Hartree–Fock exchange that is capped at 25%, thereby minimizing some of the disadvantages of Hartree–Fock exchange.

We need to stress that—despite the broadness of BC345—it still does not encompass all possible kinds of chemical applications, *e.g.*, it does not include singlet–triplet or higher-multiplet spin splitting or spin-conserving electronic excitation energies, and there is probably room for improvement in obtaining functionals with even broader good performance than the present ones.

Results for the two structural databases included in the training set are reported in the first two numerical columns of Table 5, while those for the four databases in the additional test set are reported in the last four columns. For these comparisons, we did not include the computationally inefficient global and long-range-corrected hybrid functionals (SOGGA11-X and M11), which would be very expensive for these properties, but we have added two functionals that were previously shown to have excellent performance for solid-state lattice constants: SOGGA[53] and PBEsol.[54] Table 5 shows that the performance of N12-SX and MN12-SX for lattice constants is excellent, which is important because small errors in lattice constants can lead to large errors in other properties.[16] The band gaps in the last column are approximated as crystal orbital HOMO–LUMO gaps, and they show excellent performance for N12-SX (as good as HSE06) and almost as good performance for MN12-SX (much better than the other functionals in the table).

Results in Table 5 show that both N12-SX and MN12-SX provide performances that are suitable for their application to extended systems. In all the databases of Table 5, results for

HSE06, N12-SX, and MN12-SX are similar, the biggest deviation being that HSE06 has a significantly larger error for lattice constants.

Conclusions

We presented two new functionals, N12-SX and MN12-SX combining screened-exchange with our recent nonseparable exchange-correlation terms. Both functionals provide broadly accurate performance for all chemistry and solid-state physics databases considered. N12-SX provides better performance than the popular and very successful HSE06 screened-exchange functional, while MN12-SX has the best across-the-broad performance of all the considered functionals 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 no. FA9550-11-0078.

References

1 W. Kohn, A. D. Becke and R. G. Parr, *J. Phys. Chem.*, 1996, **100**, 12974.
2 A. D. Becke, *J. Chem. Phys.*, 1997, **107**, 8554.
3 H. Schmider and A. D. Becke, *J. Chem. Phys.*, 1998, **108**, 9624.
4 P. Haas, F. Tran, P. Blaha, A. J. R. Da Silva, M. M. Odashima and K. Capelle, *Phys. Rev. B: Condens. Matter*, 2010, **81**, 125136.
5 R. Peverati and D. G. Truhlar, *J. Chem. Theor. Comput.*, 2012, **8**, 2310.
6 T. Leininger, H. Stoll, H.-J. Werner and A. Savin, *Chem. Phys. Lett.*, 1997, **275**, 151.
7 Y. Tawada, T. Tsuneda, S. Yanagisawa, T. Yanai and K. Hirao, *J. Chem. Phys.*, 2004, **120**, 8425.
8 T. Yanai, D. Tew and N. C. Handy, *Chem. Phys. Lett.*, 2004, **393**, 51.
9 O. A. Vydrov and G. E. Scuseria, *J. Chem. Phys.*, 2006, **125**, 234109.
10 R. Peverati and D. G. Truhlar, *J. Phys. Chem. Lett.*, 2012, **3**, 117.
11 Y. Zhao and D. G. Truhlar, *Theor. Chem. Acc.*, 2008, **120**, 215.
12 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.
13 N. C. Handy and A. Cohen, *Mol. Phys.*, 2001, **99**, 403.
14 J. Heyd, G. E. Scuseria and M. Ernzerhof, *J. Chem. Phys.*, 2003, **118**, 8207.
15 J. Da Silva, M. Ganduglia-Pirovano, J. Sauer, V. Bayer and G. Kresse, *Phys. Rev. B: Condens. Matter*, 2007, **75**, 045121.
16 K. Hummer, J. Harl and G. Kresse, *Phys. Rev. B: Condens. Matter*, 2009, **80**, 115205.
17 M. Schlipf, M. Betzinger, C. Friedrich, M. Ležaić and S. Blügel, *Phys. Rev. B: Condens. Matter*, 2011, **84**, 125142.
18 J. Paier, M. Marsman and G. Kresse, *J. Chem. Phys.*, 2007, **127**, 024103.
19 A. V. Krukau, O. A. Vydrov, A. F. Izmaylov and G. E. Scuseria, *J. Chem. Phys.*, 2006, **125**, 224106.
20 A. Seidl, A. Gorling, P. Vogl, J. A. Majewski and M. Levy, *Phys. Rev. B: Condens. Matter*, 1996, **53**, 3764.
21 J. Heyd, J. E. Peralta, G. E. Scuseria and R. Martin, *J. Chem. Phys.*, 2005, **123**, 174101.
22 E. N. Brothers, A. F. Izmaylov, J. O. Normand, V. Barone and G. E. Scuseria, *J. Chem. Phys.*, 2008, **129**, 011102.
23 J. W. Nicklas and J. W. Wilkins, *Appl. Phys. Lett.*, 2010, **97**, 091902.
24 S. Clark and J. Robertson, *Phys. Rev. B: Condens. Matter*, 2010, **82**, 085208.
25 T. M. Henderson, J. Paier and G. E. Scuseria, *Phys. Status Solidi B*, 2010, **248**, 767.
26 G. E. Engel, *Phys. Rev. Lett.*, 1997, **78**, 3515.
27 R. Peverati and D. G. Truhlar, *Phys. Chem. Chem. Phys.*, 2012, **14**, 13171.
28 R. Gáspár, *Acta Phys. Hung.*, 1974, **35**, 213.
29 W. Kohn and L. Sham, *Phys. Rev.*, 1965, **140**, 1133.
30 A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098.
31 A. D. Becke, *J. Chem. Phys.*, 1998, **109**, 2092.
32 Y. Zhao and D. G. Truhlar, *J. Chem. Theor. Comput.*, 2008, **4**, 1849.
33 R. Peverati and D. G. Truhlar, *J. Phys. Chem. Lett.*, 2011, **2**, 2810–2817.
34 Y. Zhao, N. E. Schultz and D. G. Truhlar, *J. Chem. Theor. Comput.*, 2005, **2**, 364.
35 S. Luo, Y. Zhao and D. G. Truhlar, *Phys. Chem. Chem. Phys.*, 2011, **13**, 13683.
36 Y. Zhao and D. G. Truhlar, *J. Phys. Chem. A*, 2005, **109**, 5656–5667.
37 Y. Zhao, N. E. Schultz and D. G. Truhlar, *J. Chem. Phys.*, 2005, **123**, 161103.
38 B. J. Lynch, Y. Zhao and D. G. Truhlar, *J. Phys. Chem. A*, 2003, **107**, 1384.
39 Y. Zhao and D. G. Truhlar, *J. Phys. Chem. A*, 2006, **110**, 10478.
40 Y. Zhao and D. G. Truhlar, *J. Chem. Phys.*, 2006, **125**, 194101.
41 E. I. Izgorodina, M. Coote and L. Radom, *J. Phys. Chem. A*, 2005, **109**, 7558.
42 R. Peverati, Y. Zhao and D. G. Truhlar, *J. Phys. Chem. Lett.*, 2011, **2**, 1991.
43 Y. Zhao, B. J. Lynch and D. G. Truhlar, *Phys. Chem. Chem. Phys.*, 2005, **7**, 43.
44 Y. Zhao, N. González-García and D. G. Truhlar, *J. Phys. Chem. A*, 2005, **109**, 2012.
45 Y. Zhao and D. G. Truhlar, *J. Chem. Theor. Comput.*, 2005, **1**, 415.
46 S. Chakravorty, S. Gwaltney, E. R. Davidson, F. Parpia and C. Fischer, *Phys. Rev. A*, 1993, **47**, 3649.
47 R. Peverati and D. G. Truhlar, *J. Chem. Phys.*, 2012, **136**, 134704.
48 R. Peverati and D. G. Truhlar, *J. Chem. Phys.*, 2011, **135**, 191102.
49 R. Li, R. Peverati, M. Isegawa and D. G. Truhlar, unpublished.
50 Y. Zhao, R. Peverati, K. Yang and D. G. Truhlar, *MN-GFM, version 6.3: Minnesota Gaussian Functional Module*, University of Minnesota, Minneapolis, 2012.
51 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr, J. E. Peralta, F. Ogiaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Revision A.1*, Gaussian, Inc., 2009.
52 K. Kudin and G. E. Scuseria, *Phys. Rev. B: Condens. Matter*, 2000, **61**, 16440.
53 Y. Zhao and D. G. Truhlar, *J. Chem. Phys.*, 2008, **128**, 184109.
54 J. P. Perdew, A. Ruzsinszky, G. I. Csonka, O. A. Vydrov, G. E. Scuseria, L. A. Constantin, X. Zhou and K. Burke, *Phys. Rev. Lett.*, 2008, **100**, 136406. Err:J. P. Perdew, A. Ruzsinszky, G. I. Csonka, O. A. Vydrov, G. E. Scuseria, L. A. Constantin, X. Zhou and K. Burke, *Phys. Rev. Lett.*, 2009, **102**, 039902.