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

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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 recently⁵ 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, N12⁵ based on a nonseparable gradient approximation (NGA) and MN12-L²⁷ 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.

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Functional form

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

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

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):

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

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

$$E_x^{\text{L-DFT}} = E_{\text{nxc}} + E_c \quad (3)$$

where the nonseparable exchange-correlation part is:

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

which contains the usual Gaspar–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:

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

$$w_{\sigma} = \frac{y_{\sigma} - 1}{y_{\sigma} + 1} \in [-1, 1].$$

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_{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 form² 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 M08³² and M11³³ 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-L²⁷ (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 ($\omega_{x\sigma} = 2.5a_0$ and $\gamma_{x\sigma} = 0.004$). 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 HSE¹⁴ functional that is sometimes called HSE06; we use the HSE06 values, *i.e.*, $X = 25$ and $\mu = 0.11a_0^{-1}$. 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 version⁵⁰ 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) algorithm⁵² 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

| <i>n</i> | Database ^a | Description | Ref. |
|----------|------------------------------|---|-------------------|
| | <i>Energetic set (BC345)</i> | | |
| 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 |
| | <i>Structural set</i> | | |
| 17 | SSLC18 | Solid state lattice constants | 10, 52 |
| 18 | DG6 | Geometries of diatomic molecules | 5 |
| | <i>Test set</i> | | |
| 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, N12⁵ and MN12-L,²⁷ as well as our recent SOGGA11-X global hybrid GGA,⁴⁸ M11 range-separated hybrid meta-GGA,³³ and HSE06¹⁹ 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 |
|-------------------------|-----------------------|
| <i>a</i> ₀₀₀ | <i>b</i> ₀ |
| <i>a</i> ₁₀₀ | <i>b</i> ₁ |
| <i>a</i> ₂₀₀ | <i>b</i> ₂ |
| <i>a</i> ₃₀₀ | <i>b</i> ₃ |
| <i>a</i> ₀₁₀ | <i>b</i> ₄ |
| <i>a</i> ₁₁₀ | <i>c</i> ₀ |
| <i>a</i> ₂₁₀ | <i>c</i> ₁ |
| <i>a</i> ₃₁₀ | <i>c</i> ₂ |
| <i>a</i> ₀₂₀ | <i>c</i> ₃ |
| <i>a</i> ₁₂₀ | <i>c</i> ₄ |
| <i>a</i> ₂₂₀ | |
| <i>a</i> ₃₂₀ | |
| <i>a</i> ₀₃₀ | |
| <i>a</i> ₁₃₀ | |
| <i>a</i> ₂₃₀ | |
| <i>a</i> ₃₃₀ | |

Table 3 Optimized parameters for the MN12-SX functional

| Exchange | Correlation |
|-------------------------|-----------------------|
| <i>a</i> ₀₀₀ | <i>b</i> ₀ |
| <i>a</i> ₀₀₁ | <i>b</i> ₁ |
| <i>a</i> ₀₀₂ | <i>b</i> ₂ |
| <i>a</i> ₀₀₃ | <i>b</i> ₃ |
| <i>a</i> ₀₀₄ | <i>b</i> ₄ |
| <i>a</i> ₀₀₅ | <i>b</i> ₅ |
| <i>a</i> ₀₁₀ | <i>b</i> ₆ |
| <i>a</i> ₀₁₁ | <i>b</i> ₇ |
| <i>a</i> ₀₁₂ | <i>b</i> ₈ |
| <i>a</i> ₀₁₃ | <i>c</i> ₀ |
| <i>a</i> ₀₁₄ | <i>c</i> ₁ |
| <i>a</i> ₀₂₀ | <i>c</i> ₂ |
| <i>a</i> ₀₂₁ | <i>c</i> ₃ |
| <i>a</i> ₀₂₂ | <i>c</i> ₄ |
| <i>a</i> ₀₂₃ | <i>c</i> ₅ |
| <i>a</i> ₀₃₀ | <i>c</i> ₆ |
| <i>a</i> ₀₃₁ | <i>c</i> ₇ |
| <i>a</i> ₀₃₂ | <i>c</i> ₈ |
| <i>a</i> ₁₀₀ | |
| <i>a</i> ₁₀₁ | |

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 |
| π TC13 | 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: SOGGA⁵³ 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-board performance of all the considered functionals for chemistry and physics and for energies and structures.

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