Exchange−Correlation Functional with Good Accuracy for Both Structural and Energetic Properties while Depending Only on the Density and Its Gradient

Roberto Peverati and Donald G. Truhlar*

Department of Chemistry and Supercomputing Institute, University of Minnesota, Minneapolis, Minnesota 55455-0431, United States

Ⓢ Supporting Information

ABSTRACT: The generalized gradient approximation (GGA) has been a workhorse exchange−correlation functional for electronic structure studies of extended systems (liquid-phase reactions, solids, heterogeneous and enzymatic catalysis, biopolymers) because its dependence on only the spin-labeled electron densities and their reduced gradients makes it the most affordable choice that produces realistic results for thermochemistry. However, much recent research has focused on its poor performance for solid-state lattice constants; the results for lattice constants can be improved but only at the cost of making the energetic predictions worse. In the present article, we propose a new density functional, called N12, which may be thought of as a generalization of range-separated functionals. The N12 functional depends only on the spin-labeled electron densities and their reduced gradients, but with a new kind of nonseparable term that gives it much greater flexibility. The N12 functional is the first exchange−correlation functional depending only on the spin-labeled electron densities and their reduced gradients that simultaneously provides good accuracy for the four key energetic and structural properties of solids and molecules, namely, solid-state cohesive energies and lattice constants and molecular atomization energies and bond lengths.

1. INTRODUCTION

Density functional theory (DFT) has achieved great success in chemistry and physics, due in large part to improvements in the necessarily approximate exchange−correlation functionals. In modern exchange−correlation functionals, the electronic energy per unit volume may depend on several properties or functionals of the electron density, both local (for example, spin densities, their gradients, and local spin kinetic energy densities) and nonlocal (such as Hartree−Fock exchange). Most functionals depending on only the spin densities and their gradients are so-called generalized gradient approximations[1] (GGAs). Adding dependence on the local spin kinetic energy densities yields meta-GGAs. Adding dependence on Hartree−Fock exchange yields hybrid functionals (which are sometimes also called hyper-GGA). Adding a dependence on unoccupied orbitals yields fifth-rung functionals.[2] Nevertheless, there is considerable interest in functionals that depend only on the spin densities and their gradients. The reasons have been nicely summarized by Fabiano et al., who said,[3] "The majority of practical DFT applications are based on GGAs and hybrid functionals, which provide the best compromise between accuracy and computational effort. In particular, GGA functionals provide an efficient tool for the study of large systems (e.g., for biology and solid-state physics) and still outperform hybrid functionals for organometallic and transition metal complexes. In addition, they attract basic theoretical interest, because they constitute the basis on which meta-GGA, hyper-GGA, and hybrid functionals are constructed."

One of the main drawbacks of the GGA functional form is that, with a single set of parameters, it cannot simultaneously provide reliable results for certain classes of noncompatible properties, and also it cannot satisfy all the known theoretical constraints. Therefore, one might choose not to enforce certain constraints in order to fit certain physical properties as well as possible.

There has been considerable recent discussion of incompatible properties, sometimes stated to be solid-state properties vs molecular properties and sometimes stated to be structural properties vs energetic properties.[3−14] (Note that solid-state physicists are often more interested in lattice constants than in cohesive energies, and chemists are often looking more for improved performance on energies than on structural parameters. But of course both communities are ultimately interested in both energy and structure. Furthermore, some authors have also connected accuracy for lattice constants with accuracy for surface energies,[5,15,16] but surface energies are beyond the scope of the present article.) Independently of precisely how they are framed, these discussions are all consistent with the observation that a single GGA cannot simultaneously provide the desired accuracy for solid-state cohesive energies, lattice constants, molecular energies, and molecular geometries. One can obtain improved performance in this regard by adding more ingredients to the functional form, e.g., by using meta-GGA functionals,[16−18] but our goal here, as motivated by the first paragraph, is to obtain good agreement for all four properties without adding ingredients. We do this by introducing a more general functional form that still depends only on spin densities and their gradients. The more general form, despite using the same ingredients, is much more flexible, and therefore it can provide reliable results for a larger number of chemical and physical systems.

No GGA has been able to provide good atomization energies for molecules and also good performance for lattice parameters of solids. Theoretical considerations and results with simple functional forms suggested[4−6,19−22] that a GGA that provides good atomization energies needs a second order coefficient in the

exchange functional that is twice as large as the exact coefficient calculated from the gradient expansion in the slowly varying limit.[23] However, this second order coefficient is one of the key ingredients to obtain correct lattice parameters in solids, and this led to the creation of functionals such as PBEsol[5,6] that intentionally sacrifice performance for molecular energies to improve the lattice constants by enforcing the second-order constraint on exchange. In a first attempt of merging the two worlds, we recently presented a GGA functional that recovers the exact second order coefficients in both exchange[23] and correlation[24] and is parametrized for broad accuracy for chemistry.[25] However, its performances for lattice constants is poor,[13] clearly showing the fact that there is more involved than simply changing the second-order coefficient. When one changes the second-order coefficient in a simple functional form, one makes global changes in the density functional that disguise the true dependencies. The approach we will take is to optimize the parameters of the new functional form against a broad set of molecular data and some solid-state data, yielding a parametrized exchange–correlation functional called N12. The parametrization process provides a systematic way to try to discover the required dependence of the density functional on its independent variables.

2. FUNCTIONAL FORM

For a spin-polarized system, a density functional approximation to the exchange energy (E_x) can be written as a function of the spin-density distributions, ρ_α and ρ_β, and their gradients $\nabla\rho_\alpha$ and $\nabla\rho_\beta$, as

$$E_x = \sum_\sigma \int d\mathbf{r}\, \Gamma_{x\sigma}(\rho_\sigma, \nabla\rho_\sigma) \tag{1}$$

where the spin variable σ is either α or β. In the popular generalized gradient approximations (GGAs), $\Gamma_{x\sigma}$ is further approximated by using a separable form:

$$\Gamma_{x\sigma}(\rho_\sigma, \nabla\rho_\sigma) = G_{x\sigma}(\rho_\sigma)\, F_{x\sigma}(x_\sigma^2) \tag{2}$$

where $G_{x\sigma}$ represents the limit for a uniform electron gas (UEG). If we set $F_{x\sigma} = 1$, we get the local spin density approximation (LSDA, with the special case of LDA for closed-shell singlets and any other systems treated as spin-unpolarized), which is calculated using the Gáspár–Kohn–Sham (GKS) formula[26,27] for the exchange energy density of the uniform electron gas (also sometimes called a free electron gas):

$$G_{x\sigma}(\rho) \equiv \varepsilon_{x\sigma}^{UEG} = -\frac{3}{2}\left(\frac{3}{4\pi}\right)^{1/3}\rho_\sigma^{4/3} \tag{3}$$

The other factor, $F_{x\sigma}$, in eq 2 is an enhancement factor that by definition depends only on even powers of the dimensionless reduced gradient, for which we use the definition of Becke:[28]

$$x_\sigma = \frac{|\nabla\rho_\sigma|}{\rho_\sigma^{4/3}} \tag{4}$$

Various approximations have been proposed for the enhancement factor for exchange, and one of the most popular is the polynomial expansion proposed in 1997 by Becke (B97),[29] where the semi-infinite variables $x_\sigma \in [0, \infty)$ are transformed into finite variables $u_{x\sigma} = \gamma_{x\sigma}x_\sigma^2/(1 + \gamma_{x\sigma}x_\sigma^2) \in [0,1]$, where $\gamma_{x\sigma}$ is a parameter, and then the enhancement factor is expanded in

formal power series of $u_{x\sigma}$:

$$F_{x\sigma}^{B97} = \sum_{i=0}^{m} a_i u_{x\sigma}^i \tag{5}$$

Going back to eq 1 for the exchange energy and following a different approach, the exchange energy can be expanded in terms of homogeneous functionals of the total density $\rho = \rho_\alpha + \rho_\beta$, as in the work of Liu and Parr.[30] As they also pointed out in their work, the viewpoint of this expansion is different, and "the argument is that atoms and molecules are far from uniform. Indeed, their essential nature is exponential falloff from nuclei. The evidence that the LDA is the best starting point is not strong". The Liu–Parr expansion of the exchange energy takes the form

$$E_x^{Liu-Parr} = \sum_{j=1}^{m} a_j\left[\int d\mathbf{r}\, \rho^{[1+(1/3j)]}\right]^j \tag{6}$$

In analogy with the formal power series expansion in the gradient variables of eq 5, a generalization of eq 6 is achieved by introducing the spin-density distributions, transforming them from semi-infinite variables $\rho_\sigma \in [0, \infty)$ to finite variables $v_{x\sigma} = \omega_{x\sigma}\rho_\sigma^{1/3}/(1 + \omega_{x\sigma}\rho_\sigma^{1/3}) \in [0,1]$, where $\omega_{x\sigma}$ is a parameter, and then by expanding the functional in a formal power series in terms of the new variables $v_{x\sigma}$:

$$H_{x\sigma} = \sum_{j=0}^{m'} a_j v_{x\sigma}^j \tag{7}$$

In the present work, we combine the formal power series expansions in $v_{x\sigma}$ and $u_{x\sigma}$ into the following functional form:

$$E_{nxc}^{NSGA} = \sum_\sigma \int d\mathbf{r}\, \Gamma_{nxc\sigma}^{NSGA}(\rho_\sigma, x_\sigma)$$
$$= \sum_\sigma \int d\mathbf{r}\, \left\{\varepsilon_{x\sigma}^{UEG} \sum_{i=0}^{m} \sum_{j=0}^{m'} a_{ij} u_{x\sigma}^i v_{x\sigma}^j\right\} \tag{8}$$

where the UEG limit (eq 3) was kept outside the summation, so that eq 8 reduces to the B97 functional form in the limiting case of $m' = 0$. Notice that this is no longer labeled as an exchange functional; in particular, we changed the subscript x to nxc to denote that in principle it is a nonseparable approximation involving both exchange and correlation; we return to this issue in the final paragraph of this section.

The integrand of eq 8 is no longer proportional to $\rho_\sigma^{4/3}F(x_\sigma)$ as in a standard GGA for exchange, where that separable form was chosen[31] to satisfy the constraint[32] on the behavior of the exact Kohn–Sham exchange energy under uniform scaling. Therefore, choosing the form of eq 8 constitutes a choice not to enforce that constraint. As discussed below, we will also not enforce the uniform-electron-gas limit for regions of large density, and we will not enforce the nonuniform scaling[33,34] constraint. To put these choices in the context of other current practices, we note that range-separated approximations to the exchange functional also fail to satisfy the uniform scaling constraint, that several approximations have been proposed that do not satisfy the uniform electron gas limit, and that few functionals satisfy the nonuniform scaling constraint. In this context, we do not want to challenge the importance of imposing exact constraints to construct functionals,[5,16,22] but rather to explore fairly unknown territory where the uniform scaling constraint is not enforced. We also note that the selective enforcement of some constraints

and not others has a long history; in fact the generalized gradient approximation was originally designed[31] in part to enforce normalization and negativity constraints on the exchange hole at the explicit expense of not enforcing the correct gradient expansion to second order, which was known not to yield accurate corrections to the UEG model.

The functional form of eq 8 can be also seen as a generalization of the dual-range GGA that we used successfully in our recent M11-L functional. See the Appendix for a discussion of this relationship.

We couple the new functional form given above with a separable B97-type functional for correlation energy (E_c). The B97-type correlation functional uses different expansions to treat the opposite-spin (OS) and same-spin (SS) contributions:

$$E_c = E_{c\alpha\beta} + \sum_\sigma E_{c\sigma\sigma}$$

(9)

where the OS contribution is calculated as

$$E_{c\alpha\beta} = \int d\mathbf{r} \, \varepsilon_{c\alpha\beta}^{\text{UEG}} \{ \sum_{i=0}^{n} b_i u_{c\alpha\beta}^i \}$$

(10)

with

$$u_{c\alpha\beta} = \frac{\gamma_{c\alpha\beta} x_{\text{avg}}^2}{1 + \gamma_{c\alpha\beta} x_{\text{avg}}^2}$$

(11)

and

$$x_{\text{avg}}^2 = \frac{1}{2}(x_\alpha^2 + x_\beta^2)$$

(12)

and the SS contribution is calculated as

$$E_{c\sigma\sigma} = \int d\mathbf{r} \, \varepsilon_{c\sigma\sigma}^{\text{UEG}} \{ \sum_{i=0}^{n'} c_i u_{c\sigma\sigma}^i \}$$

(13)

with

$$u_{c\sigma\sigma} = \frac{\gamma_{c\sigma\sigma} x_\sigma^2}{1 + \gamma_{c\sigma\sigma} x_\sigma^2}$$

(14)

The OS and SS contributions to the UEG are taken here as the Perdew–Wang parametrization,[35] using the ansatz of Stoll et al.[36,37]

For further discussion, it is useful to rewrite eq 8 as

$$E_{\text{nxc}}^{\text{NSGA}} = E^{[1]} + E^{[2]}$$

(15)

where

$$E^{[1]} = \sum_\sigma \int d\mathbf{r} \, \{ \varepsilon_{x\sigma}^{\text{UEG}} \sum_{i=0}^{m} a_{i0} u_{x\sigma}^i \}$$

(16)

and

$$E^{[2]} = \sum_\sigma \int d\mathbf{r} \, \{ \varepsilon_{x\sigma}^{\text{UEG}} \sum_{i=0}^{m} \sum_{j=1}^{m'} a_{ij} u_{x\sigma}^i v_{x\sigma}^j \}$$

(17)

We now have three options. Option 1 is to consider $E^{[1]}$ to be an exchange functional but to consider $E^{[2]}$ to be a correlation functional because it does not satisfy the uniform scaling relation for exchange. Option 1 was favored by one of the reviewers. Option 2 is to consider both $E^{[1]}$ and $E^{[2]}$ to be approximate exchange energies, while recognizing that $E^{[2]}$ does not satisfy the uniform scaling constraint. Option 2 is reasonable because

approximate functionals essentially never satisfy all known constraints, and we note that option 2 is analogous to the decision adopted by authors of range-separated exchange functionals who label approximations to the exchange functional as exchange even when they do not satisfy the uniform scaling relation. Option 3, which is the one we prefer, is to consider $E^{[2]}$ to contain both exchange and correlation, which is especially reasonable because we optimize the parameters empirically. Option 3 is also consistent with the statement that "The functionals represent exchange and correlation effects in a combined manner. Individual exchange and correlation terms cannot be isolated."[38] We note though that not everybody agrees with this statement. Consistent with option 3, when we compare our functionals to those of other workers in section 3, we will add the contributions of eqs 10, 13, 16, and 17 and simply compare the whole exchange–correlation functional.

3. SYSTEMATIC OPTIMIZATION OF THE N12 FUNCTIONAL

The general functional form of the nonseparable functional used in eq 8 has considerable flexibility to represent both exchange and correlation effects in terms of the variables ρ_σ and x_σ (or equivalently $v_{x\sigma}$ and $u_{x\sigma}$), but in order to take advantage of this, we must optimize the coefficients a_{ij}. Key elements promoting a potentially successful optimization strategy are the availability of reliable data to determine the coefficients (e.g., the training set introduced in section 3.1 below) and a good optimization procedure (this will be described in section 3.2). Using these elements, we optimize a set of parameters that yield an exchange–correlation functional called N12, whose parameters are presented in section 3.3.

3.1. Databases and Software. Many databases have been compiled and used in our group for the optimization and testing of new density functionals. The energetic training set used in this work is almost the same as the BC338 database used for the optimization of our recent M11-L meta-GGA functional;[18] the only difference is that ozone was omitted from the DC10 subdatabase to avoid to including it twice, since it is also present in the MRBE10 subdatabase. The reduced set is called BC337, which denotes a "broad chemistry" database with 337 data. In using this database, we subdivided the previous category of noncovalent complexation energies, so that the systems that are dominated by electrostatic interactions (hydrogen bonds, charge-transfer complexes, and complexes bound mainly by permanent dipole–permanent dipole interactions) can have a different weight in the optimization process than the weak interactions and the π–π stacking complexes. Thus, the subdatabase of 31 noncovalent complexation energies, NCCE31, was subdivided into EDCE19, with 19 electrostatics-dominated complexation energies, WI7/05, with seven weak interaction energies (such as rare-gas dimers), and PPS5/05, with five π–π stacking complexation energies.

Two structural databases are also used in the current training set, one with 18 solid-state lattice constants (SSLC18) and a new one with six geometries of diatomic molecules (DG6). We note that SSLC18 has a diverse group of solids: elemental solids (metals, semiconductors, and insulators) with elements from groups 1, 9, 10, 11, 13, and 14 and the second, third, fourth, and fifth periods and binary solids (semiconductors and insulators) with elemental compositions of the type 1:17, 2:16, 13:15, and 14:14 and elements from the second, third, and fourth rows of the periodic table. The diatomic molecules included in DG6 are H_2, OH, HF, N_2, Cl_2, and MgS. An overview of the databases

Table 1. Summary of the Subdatabases Used in the Current Work

#	subdatabase[a]	description	basis set[b]	weight[c]	reference(s)
		energetic set			
1	MGAE109/11[d]	main group atomization energies	MG3S	60	39, 40
2	SRMBE13	single-reference metal bond energies	def2-TZVP	5	18
3	MRBE10	multi-reference bond energies	def2-TZVP	10	18
4	IsoL6/11	isomerization energies of large molecules	MG3SXP	2	41
5	IP13/03	ionization potentials	MG3S	15	39, 42−44
6	EA13/03	electron affinities	MG3S	4	39, 42−44
7	PA8/06	proton affinities	MG3S	10	45
8	ABDE4/05	alkyl bond dissociation energies	MG3S	40	17, 39, 46
9	ABDEL8	alkyl bond dissociation energies of large molecules	MG3S	30	25, 46
10	HC7/11	hydrocarbons	6-311+G(2df,2p)	4	25
11	πTC13	thermochemistry of π systems	MG3S	50	17, 43, 45
12	HTBH38/08	hydrogen transfers barrier heights	MG3S	75	39, 47, 48
13	NHTBH38/08	non-hydrogen transfers barrier heights	MG3S	60	39, 47, 48
14	EDCE19	electrostatic dominated complexation energies	MG3S	30	42, 49, present
15	WI7/05	weak interactions	MG3S	70	42,49
16	PPS5/05	$\pi-\pi$ stacking	MG3S	70	42, 49, 50, 56
17	DC9/12[d]	difficult cases	MG3S	1	present
18	AE17	atomic energies	MG3S	5	51, 52
		structural set			
19	SSLC18	solid state lattice constants	*m*-6-311G*	18	4, 18
20	DG6	geometries of diatomic molecules	6-311+G(2df,2p)	12	present
		test set			
21	SLC34	semiconductors lattice constants	*m*-6-311G*	0	13
22	SBG31	semiconductors band gaps	*m*-6-311G*	0	13
23	SSCE8	solid-state cohesive energies	*m*-6-311G*	0	4
24	MGBL20	main group bond lengths	6-311+G(2df,2p)	0	4

[a]Details of the geometries, reference data, and basis sets used for the various subdatabases are available in the Supporting Information. [b]The references for the basis sets are MG3S,[44] def2-TZVP,[57,58] MG3SXP,[59] 6-311+G(2df,2p),[60] and *m*-6-311G*.[61] [c]Weights (w_1 to w_{18} in [cal/mol]$^{-1}$, w_{19} and w_{20} in Å^{-1}) used in the training function (eq 18), as also explained in the Supporting Information. [d]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).

used in this work, including all the corresponding references,[4,17,18,25,39−52] is available in Table 1, and more detailed information is available in the Supporting Information. Among all databases in Table 1, those with numbers 1−20 will be used in the optimization of the new functional, while databases 21−24 will be used for additional testing only.

All calculations in this article were performed with a locally modified version[53] of the *Gaussian 09* program,[54] using the ultrafine ("99,590") Lebedev grid and allowing breaking of the symmetry of the wave function in order to converge to the stable broken-symmetry solution when this is the variationally best collinear solution to the Kohn−Sham equations (through the STABLE=OPT *Gaussian* keyword). The periodic boundary conditions (PBC) algorithm[55] of *Gaussian 09* has been used to perform calculations on the solid-state physics databases.

3.2. Parametrization. The parametrization procedure must be efficient, in order to provide the best possible solution in a reasonable amount of time, systematically improvable by increasing the number of data in the training set, and not prone to numerical problems, such as spuriously oscillating functionals due to overtraining.[39,42−44,62] The formal power series expansions of eqs 8, 10, and 13 can have numerical instabilities (Runge's phenomenon), and it is therefore particularly important to keep the number of terms small and to analyze the behavior of the fitted function while the optimization proceeds, in order to limit any spurious oscillation. On the other hand, the convergence of the gradient expansion

(GE) is known to be problematic, and simple truncations at the second order are not very efficient.

A first analysis of the results based on post-SCF calculations on LSDA densities suggested that a truncation of the expansion of the exchange functional at $m = m' = 3$, for a total of 16 coefficients, is accurate enough to provide good performance without numerical instability. Both the OS and the SS expansions of the correlation (eqs 10 and 13) were truncated, after similar considerations, at $n = n' = 4$, for a total of 10 coefficients.

Since the nonseparable functional form of $E^{[2]}$ has a larger number of parameters than the separable B97 expansion, it is crucial to evaluate if the improved performance is due to a superior functional form or to overtraining (with the consequent risk of instabilities and poor performance for systems outside the training set). To explore this issue, we considered a B97 expansion and truncated it at increasingly higher numbers of terms. We noticed that already at $m = 5$ (six coefficients) the performance does not increase substantially, and the plots of the corresponding functional forms indicate numerical instabilities; at $m = 10$, the overall performance remains far from that of N12, and the functional form oscillates significantly. In contrast, the functional form of eqs 8, 10, and 13 improves the results much better with respect to the number of coefficients and maintains a reasonable behavior over its entire surface.

3.3. The N12 Functional. The functional form used here has four nonlinear parameters, $\omega_{x\sigma}$ and $\gamma_{x\sigma}$ in the nonseparable exchange-correlation terms and $\gamma_{c\alpha\beta}$ and $\gamma_{c\sigma\sigma}$ in the additional

correlation terms. The latter three occur in the B97 functional and were taken to be the same as in that functional, and $\omega_{x\sigma}$ was determined by a three-point interpolation formula using the post-SCF calculations described in the previous section. The optimization of the nonlinear parameters beyond one or two significant digits is not necessary, since the systematic refinement of the linear parameters makes the optimized functional insensitive to small changes in nonlinear parameters.

According to our own preliminary calculations at the post-SCF level, and in consideration of the numerical results obtained with the Liu and Parr expansion,[30] we decided not to enforce the UEG at higher densities, in order to obtain better performance for atomic energies. Furthermore, the main objective in designing the new exchange−correlation functional presented here is to provide good performance for both solid-state physics and chemistry, and for this reason we start from the PBEsol functional,[5,6] which has the simplest functional form that provides good performance for solid-state lattice constants. The coefficients of the $E^{[1]}$ term in eq 15 (a_{00}, a_{10}, a_{20}, a_{30}) are obtained analytically by expanding the PBEsol expression for the exchange to the third order in our gradient variable $u_{x\sigma}$ and are not fitted. The N12 nonseparable exchange−correlation enhancement factor, E_{nxc}^{NSGA}, is therefore built to reduce to PBEsol exchange in the limit of $E^{[2]} = 0$ (low densities), and the correct UEG value is enforced at $u_{x\sigma} = v_{x\sigma} = 0$ as part of the PBEsol functional form. For the B97-like correlation part, the coefficients of the zeroth-order terms are fixed to the UEG limit ($b_0 = c_0 = 1$). The remaining 20 coefficients of N12 (12 in the $E^{[2]}$ terms of eq 17 and 8 in the E_c term of eq 9) are optimized self-consistently by using a training function given by

$$F = \sum_{n=1}^{20} w_n R_n \tag{18}$$

where w_n is a fixed weight and R_n is the root mean squared error of database n (note, however, that we use the root mean squared error per bond for MGAE109 and DC9/12, see Table 1 for the details). The weights that we used in the optimization, w_n, and the corresponding number of each database, n, are both listed in Table 1. 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 and are not used in the calculation of the final performance of the functional or the functionals to which it is compared. The optimized coefficients of N12 are reported in Table 2.

In order to address the stability of the functional, we also performed sensitivity analyses on variations of the weights in the training function, and on variations of the optimized coefficients, both using N12 densities. The performances of the optimized functional were very stable on variation of the weights in the training functional (none of the mean unsigned errors significantly changed by doubling any weight in the training function), while results for the sensitivity analysis on variation of the optimized coefficients are reported in the Supporting Information.

To illustrate the new functional, we compare its exchange-correlation enhancement factor (F_{xc}) to those of other common functionals in the plots of Figure 1. We calculate and report the enhancement factors for a spin-unpolarized system ($\rho_\alpha = \rho_\beta = (1/2)\rho$) using

$$E_{xc} = \int d\mathbf{r} \, \varepsilon_x^{UEG}(\rho) \, F_{xc}(r_s, s) \tag{19}$$

Table 2. Optimized Parameters (in Atomic Units) for the N12 Functional

	exchange		correlation
$\omega_{x\sigma}$	2.5	opposite spin	
$\gamma_{x\sigma}$	4×10^{-3}	$\gamma_{c\alpha\beta}$	6×10^{-3}
a_{00}	1	b_0	1
a_{10}	5.07880×10^{-1}	b_1	-5.53170
a_{20}	1.68233×10^{-1}	b_2	3.07958×10
a_{30}	1.28887×10^{-1}	b_3	-5.64196×10
a_{01}	8.60211×10^{-2}	b_4	3.21250×10
a_{11}	-1.71008×10		
a_{21}	6.50814×10	same spin	
a_{31}	-7.01726×10	$\gamma_{c\sigma\sigma}$	2×10^{-1}
a_{02}	-3.90755×10^{-1}	c_0	1
a_{12}	5.13392×10	c_1	3.24511
a_{22}	-1.66220×10^2	c_2	-2.52893×10
a_{32}	1.42738×10^2	c_3	1.44407×10
a_{03}	4.03611×10^{-1}	c_4	1.96870×10
a_{13}	-3.44631×10		
a_{23}	7.61661×10		
a_{33}	-2.41834		
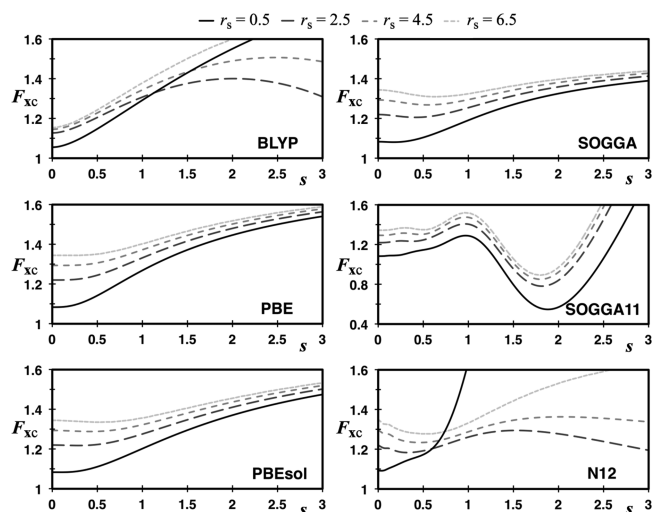
Figure 1. Enhancement factors of different exchange−correlation functionals for spin-unpolarized systems, as a function of reduced density gradient s, for various values of the Wigner-Seitz radius in bohrs (r_S/a_0). All functionals except SOGGA11 are on the same scale.

where s is the dimensionless reduced gradient according to Perdew's notation,[31] which in the spin-unpolarized case takes the form

$$s = \frac{|\nabla \rho|}{2(3\pi^2)^{1/3} \rho^{4/3}} \tag{20}$$

and r_S is the Wigner−Seitz radius defined by

$$r_S = \left(\frac{3}{4\pi\rho}\right)^{1/3} \tag{21}$$

The enhancement factors are calculated and plotted in key ranges of interest for real systems, in particular $0 \leq s \leq 3$ and $0.5 \leq r_S/a_0 \leq 6.5$.

4. PERFORMANCE OF THE N12 FUNCTIONAL

We analyze the performance of the new functional on several databases representative of classes of chemical and physical

properties. Since N12 is a functional of the density and its reduced gradient, we focus the comparison on GGA approximations, but we include also some meta-GGA functionals (simply labeled "meta" in the tables) and two hybrids. The functionals that we considered are one LSDA, GKSVWN5;[26,27,63] 13 GGAs: OLYP,[64,65] BPW91,[28,66] RPBE,[67] HCTH407,[68] mPWPW,[69] revPBE,[70] BLYP,[28,65] PW91,[66] BP86,[1,28] PBE,[22] PBEsol,[5,6] SOGGA,[4] and SOGGA11;[25] three conventional meta-GGAs, TPSS,[71] revTPSS,[16] and M06-L;[17] one range-separated meta-GGA, M11-L;[18] one screened-exchange hybrid GGA, HSE;[72] and one global hybrid GGA, B3LYP.[65,73,74] Note that all of the functionals considered in this list are based purely on local ingredients except for the two hybrid functionals. Among these hybrid functionals, however, only HSE is suitable for solid-state calculations, since it does not include the computationally expensive nonlocal Hartree–Fock exchange at large interelectronic separations. Depending on the problem and the computer program, calculations with HSE still can be more expensive than those with local functionals by a factor between two and five with *Gaussian 09* (but for at least some plane waves codes, this factor can be as big as 2 orders of magnitude). B3LYP calculations with periodic boundary conditions are very expensive, and therefore we will report B3LYP results only for the chemistry databases.

Table 3 compares the overall energetic performance of each functional in terms of the mean unsigned error (MUE) for the BC337 energetic database and its subdatabases and subsets. In order to make the key trends more visible, we placed the N12 column in bold, and for each subdatabase listed we put the three smallest mean unsigned errors of GGAs in bold. No single number or even a set of numbers can fully capture all the good and bad aspects of performance, but in addition to BC337, we also include BC320xAE, which is averaged over all the data of BC337 except the 17 atomic energies. One reason to separate the atomic energies is that our basis set does not have enough flexibility in the core for the atomic energies to be converged with respect to basis set.

Table 3 shows that N12 is better than any GGA to which it is compared in three categories (MRBE10, ABDE4, and EDCE19), is bested by only one GGA in two other categories (IsoL6 and HC7), and is better than all but two in four other categories (MGAE, PA8, ABDEL8, and DC9/12). Because of good across-the-board performance, it does quite well for the two bottom lines. In particular, from the overall results for the broad chemistry energetic database (BC337), it emerges that OLYP and SOGGA11 are the best performing GGAs to which we compare, followed by HCTH407, but N12 has a smaller mean unsigned error than any of them for this diverse energetic database.

We turn next to the structural databases in Table 4. Again we put N12 in bold, and the three smallest MUEs—among functionals that depend only on local densities and density gradients—for each subdatabase in bold. Here, we see that only two of the GGAs to which we compare, namely, PBEsol and SOGGA, have acceptable errors for the diverse solid state lattice constants (SSLC18), and N12 is as good as SOGGA and better than PBEsol. Furthermore, returning to Table 3, we see that SOGGA and PBEsol had the two worst mean errors for energetic quantities, but N12 had the second best. So whereas none of the GGAs to which we compare is good for both molecular energetics and solid-state lattice constants, N12 is good for both.

Table 4 also includes the diatomic geometries database. For this database, N12 is bested by only HCTH407, which (as seen in Table 3) also does quite well for molecular energetics. It is very

interesting to see that HCTH407, OLYP, and SOGGA11 do poorly for solid-state lattice constants but quite well for diatomic geometries, whereas N12 does well for both. Notice that the errors in lattice constants are larger than the error in bond lengths, but that is partly a consequence of the way lattice constants are defined. As presented in detail in the Supporting Information, the lattice constants are usually larger than the nearest neighbor distances—in fact, for the SSLC18 database (and similarly for SLC34), they are larger on average by a factor of 2.1. All other things being equal, one would expect the MUEs for the lattice constants to be larger than those for molecular bond lengths by a factor of about 2.

Another interesting comparison is between the errors for the atomic energies subdatabase, AE17 in Table 3, and that for the lattice constants subdatabase, SSLC18 in Table 4. The best functionals for the lattice constants, PBEsol and SOGGA, are the worst functionals for the atomic test set, while those that have best performances for the atoms, OLYP and SOGGA11, are the worst for lattice constants. This is even clearer by comparing the performances of the PBE and PBEsol functionals, which share common forms but have parameters that are optimized to provide either good chemistry (PBE) or good solid-state physics (PBEsol). The performance for the atomic energies set is highly influenced by the associated change of parameters, with the error of PBEsol about 5 times larger than that of PBE for the AE17 set. Even at the meta-GGA level, using similar functional forms with coefficients that provide better lattice constants significantly worsens the performance for the atomic energies, as can be seen comparing the TPSS and revTPSS functionals. Notably, the AE17 performance is the only subdatabase that is significantly affected by this change of parameters; for all other subdatabases, revTPSS is either very similar to or slightly superior to TPSS, whereas the atomic energies are worse by a factor of about 2. N12 is the only exception to this trend, and it performs well for both the SSLC18 and AE17 sets. A more complete assessment of atomic energies would involve basis sets with more flexibility in the core regions.

Next consider Table 5, where again we have bolded the N12 results and the three smallest MUEs for gradient-based functionals for each database. The first set of results is for 34 semiconductor lattice constants; only five of these were used in training. It is encouraging to again see excellent results for N12. A similar situation holds for the last column of Table 5.

Band gap calculations with DFT do not stand on solid theoretical grounds because any Kohn–Sham potential—even the exact one—will not lead to accurate band structures, because it omits the contribution from the derivative discontinuity.[75] Nevertheless, predictions of band gaps are important and a very active research topic,[13,61,76−83] so we present band gaps for their practical interest value. The band gaps column in Table 5 shows N12 performs in a below average way for semiconductor band gaps, although it does do better than the only two GGAs that do well for lattice constants (PBEsol and SOGGA). This shows that getting good lattice constants is still incompatible with getting good semiconductor band gaps.

The SSCE8 database in Table 5 measures performance for solid-state cohesive energies. N12 does reasonably well, with a MUE 9 times smaller than revPBE, 5 times smaller than RPBE, 4 times smaller than PW91, and 3 times smaller than OLYP and BLYP.

The discussion above focused on a comparison of N12 to GGAs. It is also of interest to consider comparison to meta-GGAs, which are also local but have one more kind of ingredient

Table 3. MUEs (kcal/mol) for the BC337 Energetic Set and Its Subsets[a]

type	LSDA	GGA	GGA	GGA	GGA	GGA	GGA	GGA	GGA	GGA	GGA	GGA	GGA	GGA	present	meta	meta	meta	meta	hybrid	hybrid
functional	GKSVWN5[a]	SOGGA	PBEsol	PBE	BP86	PW91	BLYP	mPWPW	revPBE	BPW91	RPBE	HCTH407	SOGGA11	OLYP	N12	TPSS	revTPSS	M06-L	M11-L	B3LYP	HSE
no. of fitted parameters	...	...	...	...	1	...	1	2	1	1	...	18	18	2	21	...	...	38	49	3	1
MGAE109/11[b]	16.75	7.82	7.94	3.07	3.65	3.23	1.54	2.05	1.68	1.40	1.99	1.12	1.68	0.91	1.27	1.07	0.94	0.87	0.74	0.99	0.88
SRMBE13	10.47	5.44	5.46	3.61	3.71	4.60	3.02	3.30	3.10	3.69	3.13	3.37	6.26	4.82	4.56	2.91	3.28	3.40	3.21	2.73	2.35
MRBE10	41.18	23.99	27.12	19.27	17.86	19.92	17.72	17.73	9.33	16.41	8.79	10.11	14.30	7.61	6.65	10.60	11.35	9.97	6.14	22.44	25.09
IsoL6/11	2.05	1.89	1.55	1.98	2.28	1.92	3.73	2.16	2.82	2.38	2.99	3.02	1.73	3.44	1.73	3.66	3.96	2.76	1.57	2.61	1.25
IP13/03	5.49	2.48	2.66	3.62	5.43	4.54	4.81	4.19	3.07	3.74	3.12	5.46	4.74	2.60	3.14	3.09	2.96	3.08	3.11	4.76	3.23
EA13/03	5.70	2.70	2.16	2.27	4.21	2.60	2.68	2.30	2.39	2.26	2.37	3.70	5.23	3.60	3.89	2.35	2.59	3.83	5.54	2.33	2.77
PA8/06	5.07	2.33	2.10	1.34	1.41	1.30	1.58	1.52	2.00	1.88	1.98	2.84	2.11	2.40	1.35	2.66	2.79	1.88	2.17	1.02	1.10
ABDE4/05	15.84	5.09	4.03	4.09	6.16	3.82	10.60	6.31	10.59	8.37	11.21	9.05	5.00	10.28	3.81	9.56	7.64	5.54	5.14	8.73	5.82
ABDEL8	11.74	3.87	3.18	7.16	8.09	6.80	12.18	9.01	12.94	10.85	13.49	11.61	7.89	12.12	6.54	10.93	9.02	8.85	6.98	10.40	8.70
HC7/11	21.45	17.88	13.31	3.97	9.95	4.55	27.39	8.08	13.65	10.77	14.96	14.97	6.26	17.01	4.27	10.48	6.42	3.35	2.42	16.80	7.34
πTC13	5.40	4.72	4.84	6.01	6.24	6.14	6.42	6.72	7.34	7.29	7.38	8.25	7.61	8.32	8.69	8.16	7.93	6.52	5.47	6.06	6.17
HTBH38/08	17.55	12.88	12.69	9.31	9.16	9.60	7.52	8.43	6.58	7.38	6.43	5.48	6.57	5.63	6.94	7.71	6.96	4.15	1.44	4.23	4.23
NHTBH38/08	12.42	9.68	9.86	8.42	8.72	8.80	8.53	8.03	6.82	7.26	6.82	6.29	4.32	5.25	6.86	8.91	9.07	3.81	2.86	4.55	3.73
EDCE19	4.79	2.45	2.35	1.29	1.14	1.56	1.28	1.13	1.46	1.40	1.37	1.18	1.68	2.50	1.07	1.06	1.08	0.77	0.67	0.70	0.71
W17/05	0.30	0.13	0.10	0.14	0.65	0.27	0.45	0.24	0.32	0.71	0.24	0.29	0.91	0.39	0.42	0.20	0.18	0.17	0.31	0.30	0.13
PPS5/05	0.60	1.55	1.66	2.23	3.63	1.81	4.01	2.99	3.91	4.17	3.54	2.14	0.36	4.97	3.25	2.74	2.45	0.21	0.43	2.89	1.65
DC9/12[b]	157.24	8.34	8.06	3.85	3.81	3.98	2.71	2.86	3.43	2.51	3.75	3.48	3.00	3.26	2.73	1.95	2.28	2.36	1.03	2.40	1.97
AE17	429.05	290.38	253.24	54.44	13.70	7.78	8.67	9.62	15.51	8.35	7.99	12.86	6.99	6.89	8.41	13.61	27.03	3.86	7.22	13.62	39.56
BC337[c]	38.27	22.02	20.13	7.49	5.95	5.39	5.23	4.89	4.78	4.56	4.52	4.45	4.12	4.03	3.91	4.73	5.20	2.87	2.37	4.20	5.08
BC320xAE[c]	17.51	7.77	7.74	4.99	5.54	5.26	5.04	4.64	4.21	4.36	4.33	4.01	3.97	3.88	3.67	4.26	4.04	2.82	2.12	3.70	3.25

[a]The exchange calculated as in eq 3, also referred to as local spin density approximation exchange, plus VWN correlation number 5. [b]Errors for MGAE109/11 and DC9/12 are reported on a per bond basis, as explained in Table 1. [c]The overall mean unsigned errors are calculated by using eq S3 of the Supporting Information.

Table 4. Mean Unsigned Errors (Å) for the Structural Set and Its Subsets

functional	type	SSLC18	DG6
GKSVWN5	LSDA	**0.056**	0.011
SOGGA	GGA	**0.021**	**0.009**
PBEsol	GGA	**0.025**	0.010
PBE	GGA	0.067	0.013
BP86	GGA	0.071	0.015
PW91	GGA	0.081	0.012
BLYP	GGA	0.113	0.022
mPWPW	GGA	0.070	0.013
revPBE	GGA	0.108	0.016
BPW91	GGA	0.076	0.013
RPBE	GGA	0.109	0.017
HCTH407	GGA	0.120	**0.004**
SOGGA11	GGA	0.122	**0.008**
OLYP	GGA	0.121	**0.009**
N12	present	**0.021**	**0.008**
TPSS	meta	0.054	0.011
revTPSS	meta	0.034	0.011
M06-L	meta	0.071	0.006
M11-L	meta	0.050	0.011
HSE	hybrid	0.035	0.003

Table 5. Mean Unsigned Errors for the Test Set (Lattice Constants and Bond Lengths Are in Å, Band Gaps in eV, and Cohesive Energies in eV/atom)

functional	type	SLC34	SBG31	SSCE8	MGBL20
GKSVWN5	LSDA	**0.037**	1.14	0.70	0.010
SOGGA	GGA	**0.027**	1.14	0.27	0.010
PBEsol	GGA	**0.035**	1.14	0.31	0.010
PBE	GGA	0.097	0.98	**0.11**	0.010
BP86	GGA	0.107	1.12	0.12	0.011
PW91	GGA	0.094	1.11	0.50	0.008
BLYP	GGA	0.178	1.14	0.37	0.013
mPWPW	GGA	0.101	1.11	**0.10**	0.009
revPBE	GGA	0.140	1.08	1.12	0.012
BPW91	GGA	0.100	1.10	0.20	0.009
RPBE	GGA	0.155	1.07	0.61	0.013
HCTH407	GGA	0.160	**0.89**	0.30	**0.004**
SOGGA11	GGA	0.104	**0.89**	**0.07**	**0.006**
OLYP	GGA	0.149	**0.90**	0.36	**0.007**
N12	present	**0.035**	0.99	**0.13**	**0.008**
TPSS	meta	0.083	0.85	0.22	0.007
revTPSS	meta	0.061	1.00	0.13	0.008
M06-L	meta	0.088	0.73	0.17	0.004
M11-L	meta	0.071	0.54	0.24	0.010
HSE	hybrid	0.051	0.26	0.11	0.006

(spin kinetic energy densities), and such comparisons are made in Tables 3−5. N12 is better than both TPSS and the very recent revTPSS for multireference bond energies, isomerization energies of large molecules, proton affinities, both sets of alkyl bond dissociation energies, hydrocarbon energetics, both barrier height subdatabases, atomic energies, the overall broad chemistry database (with or without including atomic energies), solid-state and semiconductor lattice constants, and the diatomic geometry subdatabase. For the solid-state cohesive energies, it does better than TPSS and the same as revTPSS. This is quite remarkable considering the smaller number of ingredients. N12 even does better than the hybrid HSE for several properties, namely multireference bond energies, both alkyl bond dissociation

energy databases, hydrocarbon energetics, and solid-state and semiconductor lattice constants.

5. CONCLUDING REMARKS

In order to place the new N12 exchange−correlation functional in perspective, we consider the four key energetic and structural properties of solids and molecules, namely, solid-state cohesive energies and lattice constants and molecular atomization energies and bond lengths. Table 6 provides a direct comparison

Table 6. Close comparison of MUEs of GGAs for key properties

functional	solids energies[a]	solids structures[b]	molecules energies[c]	molecules structures[d]
SOGGA	0.27	**21**	7.82	**10**
PBEsol	0.31	**25**	7.94	**10**
PBE	**0.11**	67	3.07	**10**
PW91	0.50	55	3.23	**8**
mPWPW	**0.10**	65	2.05	**9**
BPW91	0.20	76	**1.40**	**9**
RPBE	0.61	109	1.99	13
HCTH407	0.30	114	**1.12**	**4**
SOGGA11	**0.07**	122	**1.68**	**6**
OLYP	0.36	115	**0.91**	7
N12	**0.13**	21	1.27	8

[a]SSCE8 in eV/atom. [b]SSLC18 in milliÅ. [c]AE109/11 in (kcal/mol)/bond. [d]MGBL20 in milliÅ

with GGAs for these databases; the GGAs listed are the ones that have either the lowest, second lowest, or third lowest MUE for one or more of the four key properties. We bolded the MUE values that we consider satisfactory. Only N12 is satisfactory for all four key properties.

■ APPENDIX: THE FUNCTIONAL FORM USED FOR THE NONSEPARABLE PART OF N12 AS A GENERALIZATION OF RANGE SEPARATION

In the limit where the kinetic energy density is approximated by its UEG limit (the limit of $w = 0$ in the notation of ref 18), the exchange enhancement factor of the dual-range meta-GGA of M11-L reduces to a dual-range GGA exchange functional that is equivalent to using

$$F_{x\sigma}^{M11\text{-}GGA} = G^{LSDA}(\alpha(\rho^{1/3}); \omega)[a_0^{SR\text{-}X} F_x^{PBE}(s) + b_0^{SR\text{-}X} F_x^{RPBE}(s)]$$
$$+ [1 - G^{LSDA}(\alpha(\rho^{1/3}); \omega)]$$
$$\times [a_0^{LR\text{-}X} F_x^{PBE}(s) + b_0^{LR\text{-}X} F_x^{RPBE}(s)] \qquad (A1)$$

where the dependence of G^{LSDA} on α and of α on $\rho^{1/3}$ are given in ref 18; G^{LSDA} also depends on a parameter ω. The $\{a_0^X\}$ and $\{b_0^X\}$ are also parameters, and F_x^{PBE} and F_x^{RPBE} are GGA enhancement factors according to the PBE[22] and RPBE[67] approximations. The key point about eq A1 is that it has a nonseparable form; that is, the gradient enhancement depends on the value of ρ. The particular range-defining function[84,85] of ρ that controls which of the gradient enhancements is used is justified by range separation[86] of the LSDA exchange. In the present work, rather than limit ourselves to range-defining functions like G^{LSDA} that are justified by range separation of the interelectronic repulsion operator, we effectively optimize the range-defining function by using a general nonseparable form, eq 8.

For further insight, we can plot G^{LSDA} as a function of the density and compare it to the simpler expression $v_{X\sigma} = (\omega_{X\sigma}\rho_\sigma^{1/3})/(1 + \omega_{X\sigma}\rho_\sigma^{1/3})$, which is the basic term in the N12 functional, as in Figure 2. The range-separation curve with the Yukawa
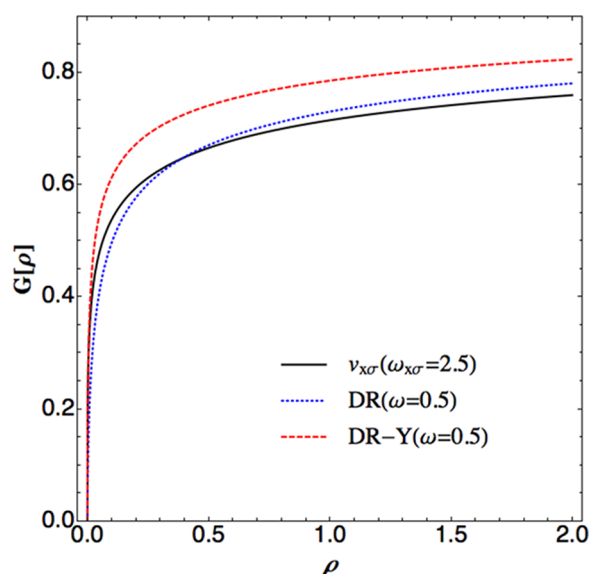

Figure 2. The $v_{x\sigma}$ term of N12 (solid, black) as a function of the density, compared to the dual-range separation (blue, dotted) and the dual-range with Yukawa potential (red, dashed).

potential[87−89] was also calculated and reported in the plots of Figure 2, to show how well N12 can be justified as being like a more flexible form of range separation.

ASSOCIATED CONTENT

Ⓢ Supporting Information
Subdatabases of BC337, details of the calculation and results, and Fortran routines for the N12 functional. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author
*E-mail: truhlar@umn.edu
Notes
The authors declare no competing financial interest.

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