Improved constraint satisfaction in a simple generalized gradient approximation exchange functional

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Though there is fevered effort on orbital-dependent approximate exchange-correlation functionals, generalized gradient approximations, especially the Perdew-Burke-Ernzerhof (PBE) form, remain the overwhelming choice in calculations. A simple generalized gradient approximation (GGA) exchange functional [A. Vela, V. Medel, and S. B. Trickey, J. Chem. Phys. **130**, 244103 (2009)] was developed that improves substantially over PBE in energetics (on a typical test set) while being almost as simple in form. The improvement came from constraining the exchange enhancement factor to be below the Lieb-Oxford bound for all but one value of the exchange dimensionless gradient, s, and to go to the uniform electron gas limit at both $s = 0$ and $s \to \infty$. Here we discuss the issue of asymptotic constraints for GGAs and show that imposition of the large s constraint, $\lim_{s\to\infty} s^{1/2} F_{xc}(n, s) < \infty$, where $F_{xc}(n, s)$ is the enhancement factor and n is the electron density, upon the Vela-Medel-Trickey (VMT) exchange functional yields modest further improvement. The resulting exchange functional, denoted VT{8,4}, is only slightly more complicated than VMT and easy to program. Additional improvement is obtained by combining VT{8,4} or VMT exchange with the Lee-Yang-Parr correlation functional. Extensive computational results on several datasets are provided as verification of the overall performance gains of both versions. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.3701132]

I. SETTING

Despite the popularity of both exact exchange and hybrid exchange-correlation functionals (which include an exact-exchange contribution), and the insights into density functional theory that such functionals provide, their explicit orbital dependence introduces significant computational burden. The burden is particularly problematical for the computation of Born-Oppenheimer forces at each step of a molecular dynamics simulation. Thus, there is motivation to seek improvement of simpler approximate functionals, even though that subject has been rather well combed-over in the last two decades.[1] Having demonstrated substantial error reduction for molecular atomization energies (at comparatively modest cost in bond length errors) with a simple, non-empirical, constraint-based generalized gradient exchange functional,[2] E_{xVMT}, combined with the Perdew-Burke-Ernzerhof (PBE) (Ref. 3) correlation functional, E_{cPBE}, we set out to impose further constraints in search of additional improvements.

Concurrently, we undertook study of the effect of using a different correlation functional, the Lee-Yang-Parr (LYP) functional,[4] E_{cLYP}. An encouraging precedent in this connection is the work of Adamo and Barone.[5] They found that the combination of the Lacks-Gordon[6] exchange functional with E_{cLYP} gave quite good results for a reasonably large, diverse test suite of molecules. The relevance to our work is that E_{xLG} was constructed and parameterized semi-empirically to satisfy two asymptotic constraints we use. However, its qualitative behavior is quite different, thereby providing the potential for insight into the consequences of such differences.

To set notation, we recall that a generalized gradient approximation (GGA) exchange functional can be written conveniently in terms of an enhancement factor F_x with respect to the simplest local exchange, to wit

$$E_x[n] = \int d\mathbf{r}\, n(\mathbf{r})\, \varepsilon_{xLDA}[n(\mathbf{r})]\; F_x[s(\mathbf{r})],$$
$$\varepsilon_{xLDA}[n(\mathbf{r})] := C_x\, n^{1/3}(\mathbf{r}), \tag{1}$$
$$C_x := -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3},$$

where the dimensionless reduced gradient s is given by

$$s(\mathbf{r}) = \frac{|\nabla n|}{2(3\pi^2)^{1/3} n^{4/3}}. \tag{2}$$

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The PBE form[3] is perhaps the most heavily used GGA today. Numerical values of PBE parameters arise purely from satisfaction of a selected set of exact constraints (global, bounds, and limits). However, it is demonstrable (see discussion below) that there are more constraints than can be satisfied by a GGA form, so constraint-based construction inevitably involves choices. A notable example is imposition of the Lieb-Oxford (LO) bound,[7]

$$\frac{E_{xc}[n]}{E_{xLDA}[n]} \leq \lambda_{LO}, \qquad E_{xLDA}[n] = \int d\mathbf{r}\, n(\mathbf{r})\, \varepsilon_{xLDA}[n(\mathbf{r})]. \tag{3}$$

Regarding this bound, the choice is global satisfaction (necessary) versus local satisfaction (sufficient). Local satisfaction requires $F_x \leq \lambda_{LO}$ in Eq. (1). This is much easier to employ in functional construction than the global bound, Eq. (3). In particular, to ensure that an approximate functional is universal, such local (point-wise) enforcement seems to be the only practical option. The original LO value of the bounding constant is $\lambda_{LO} = 2.2733$. There has been off and on discussion of lower values.[8] More recently, substantial evidence that the *de facto* ratio in real systems is markedly below the value $\lambda_{LO} = 2.2733$ has been amassed. See the detailed discussion and references in Ref. 2 as well as the original papers.[9–11]

In recognition of this non-exhaustion of the LO bound in real systems, the Vela-Medel-Trickey (VMT) X-functional introduced in Ref. 2 enforces the LO bound point-wise,

$$F_{xVMT} := 1 + \frac{\mu s^2\, e^{-\alpha\, s^2}}{1 + \mu s^2}. \tag{4}$$

The parameter α is chosen by local satisfaction of the LO bound, with equality, $F_{xVMT} = \lambda_{LO}$, at only one point. This is done by adjusting α such that the unique maximum (for $s \geq 0$) equals the LO bound for the chosen value of μ. In turn, μ was set[2] by use of the PBE correlation functional, E_{cPBE}, with either the original PBE value, $\mu_{PBE} = 0.21951$, or the gradient-expansion value,[12] $\mu_{GE} = 10/81 \approx 0.123457$, as used in the PBEsol functional.[13,14] The original PBE choice gives correct local spin density (LSD) linear response in the limit $s \to 0$ by cancellation of the quadratic term (in that limit) from E_{cPBE}. The PBEsol modification uses the gradient-expansion value in recognition of its pertinence to extended systems at the cost of not satisfying the small s limit linear response. See Refs. 13 and 14 for detailed discussion. Use of PBE or PBEsol correlation with VMT exchange and suitably chosen μ gives the VMT analogs to PBE and PBEsol. Note that in Ref. 2, only PBE correlation was used, irrespective of μ.

II. IMPROVED ASYMPTOTIC BEHAVIOR

Consider a non-spin-polarized system. A key argument in developing the VMT form, Eq. (4), is that because large values of s can correspond to regions of small values of both the density and its gradient, not large density gradients (related discussion is found in Refs. 15–17), one could expect that in these small-gradient, low-density regions the enhancement function would be rather close to that of a uniform electron gas. This possibility rationalizes the large-s VMT behavior, namely,

$$\lim_{s\to\infty} F_{xVMT}(s) \to 1. \tag{5}$$

Though appealing on these grounds, Eq. (5) still violates the exact asymptotic requirement,[18]

$$\lim_{s\to\infty} s^{1/2} F_{xc}(n,\ s) < \infty. \tag{6}$$

Observe that, for spatially uniform spin-polarization, a GGA exchange-correlation functional may be written exactly in terms of an enhancement factor with respect to local exchange. That enhancement factor may be rewritten as

$$F_{xc}(n,\ s) = F_x(s) + F_c(n,\ s), \tag{7}$$

so that the asymptotic requirements are

$$\lim_{s\to\infty} s^{1/2} F_x(s) < \infty, \tag{8}$$

and

$$\lim_{s\to\infty} s^{1/2} F_c(n,\ s) < \infty. \tag{9}$$

With respect to the exchange limit given by Eq. (8), neither VMT nor PBE, and its revisions,[19,20] satisfy this constraint. To our knowledge, the only published GGA X-functionals which do respect Eq. (8) are the widely used PW91 (Ref. 21) and the semi-empirical Lacks and Gordon X-functional (LG) already noted.[6]

There is another finite-system asymptotic constraint upon the exchange energy density,

$$\lim_{r\to\infty} \varepsilon_x = -n(\mathbf{r})/2r. \tag{10}$$

For a GGA, it is equivalent[22] to requiring

$$\lim_{s\to\infty} F_{xGGA}(s) \to s/\ln s. \tag{11}$$

Equations (8) and (11) of course are incompatible. However, it has been shown[23] that Eq. (11) does not have a meaningful influence on the accuracy of calculated exchange energies. Thus, we choose to enforce Eq. (8) because it is relevant to point-wise satisfaction of the LO bound.[21,22] Equation (8) is satisfied if we modify the VMT form to read

$$F_{xVT\{m,n\}}(s) = F_{xVMT}(s) + \left(1 - e^{-\alpha\, s^{m/2}}\right)\left(s^{-n/2} - 1\right) = 1 + \frac{\mu\, s^2\, e^{-\alpha\, s^2}}{1+\mu\, s^2} + \left(1 - e^{-\alpha\, s^{m/2}}\right)\left(s^{-n/2} - 1\right), \tag{12}$$

where m and n are positive integers. Just as in VMT, μ is to be determined by compatibility with the correlation functional and α is to be set by having the maximum of $F_{xVMT\{m,n\}}$ equal to λ_{LO}. We assume that m and n are positive integers and determine them from the following requirements. To recover uniform electron gas behavior requires that $\lim_{s\to 0} F_x(s) = 1$. For small s, the leading terms in the expansion of F_x must be quadratic. On grounds of rotational invariance (as well as smoothness), the series expansion of the enhancement function must contain only even powers of s. From these requirements, one finds the following conditions:

$$m > n, \tag{13a}$$

TABLE I. Values of α for VT{8,4}, Eq. (12), and VMT, Eq. (4), exchange enhancement factors for two values of the parameter μ.

	μ	$\alpha_{VT\{8,4\}}$	α_{VMT}
GE	10/81	0.000023	0.001553
PBE	0.219516	0.000074	0.002762

$$m/2 \text{ and } (m-n)/2 \text{ must be even.} \tag{13b}$$

From the admissible integer pairs defined by these requirements, we must select a particular pair. At this point, design criteria enter. For moderately large, finite s, the desired behavior is to be as close as possible to F_{xVMT}, in order to preserve its improved performance over PBE. Specifically, for about $15 \leq s \leq 50$, the enhancement factor should go over smoothly (without physically meaningless kinks, bumps, or other oddities) to $F_{xVT\{m,n\}} \approx 1$. The result is $m = 8$, $n = 4$. While this result is a consequence of design criteria as well as rigorous constraints, we emphasize that the values {8,4} were not obtained on the basis of any empirical parameterization to chemical or physical data but from the Occam's razor criterion. Only after fixing $\{m,n\} = \{8,4\}$, did we do the comparative numerical studies reported here. Thus, $F_{xVT\{8,4\}}$ is an entirely non-empirical functional. (Remark: we use the notation {8,4} to distinguish from the two-digit year-of-introduction convention widely used in labeling functionals, e.g., PW91).

Though, as mentioned above, values of λ_{LO} significantly smaller than the original one have been discussed rather persuasively,[9–11] we elected to retain strict constraints, hence used the original value,[7] 2.2733. Then, for both values of μ, either the original in PBE ($\mu_{PBE} = 0.219516$) or the gradient expansion as used in PBEsol ($\mu_{GE} = 10/81$), a value of α ensues. The results for both VT{8,4} and VMT are summarized in Table I. Figure 1 provides a comparison of $F_{xVT\{8,4\}}$ for the PBE value of μ with F_{xVMT}, F_{xPBE}, F_{xPW91}, and F_{xLG}. One sees that the LG functional samples values of the s variable rather differently than either PBE or PW91. Thus, those three functionals provide a useful comparative spectrum of constraint-based GGAs for the present study.

For μ_{PBE}, Fig. 1 shows that both the VT{8,4} and VMT enhancement factors are above the PBE and PW91 factors in

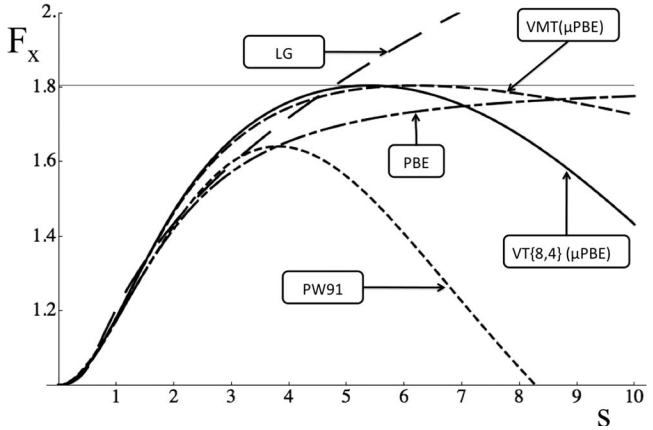

FIG. 1. Comparison of exchange enhancement factors $F_{xVT\{8,4\}}$, F_{xVMT}, F_{xPBE}, (all three for μ_{PBE}), F_{xPW91}, and F_{xLG}.

the interval $1 \leq s \leq 7$. While VT{8,4} does vaguely resemble PW91 (both satisfy Eqs. (3) and (8) and each has a maximum), quantitatively the two are quite different. VT{8,4} provides a much stronger enhancement. The relationship differs for μ_{GE} (see Figure S1 in the supplementary material[28]). For that value, $F_{xVT\{8,4\}}$ stays close to $F_{xPBEsol}$ at small s and below F_{xPW91}. Then, it goes above F_{xPW91} at around $s \approx 4$ and stays above $F_{xPBEsol}$ until $s \approx 9$.

The remaining issue of functional development is E_c where, again, design criteria enter. In this study, we chose three functionals. One choice is the original PBE correlation functional, E_{cPBE}. The second choice is to use this latter functional but fixing the β parameter, which is the coefficient of the quadratic contribution, to cancel the corresponding term in the PBEsol exchange. This leads to a value of $\beta = 0.0375$, which is slightly smaller than the fitted value used in the correlation of PBEsol, where $\beta = 0.046$.[14] To emphasize this difference, this correlation functional will be designated as $E_{cPBE\text{-}GE}$. To test if the PBE correlation-type functionals (E_{cPBE}, $E_{cPBEsol}$, *or* $E_{cPBE\text{-}GE}$) satisfy Eq. (9), the corresponding expression for F_C, as a function of r_s and s, was evaluated with Mathematica, to establish the $\lim_{s\to\infty} s^{1/2} F_c(n,\ s)$ for a given value of r_s, which fixes the local value of n (**r**). For both the spin-unpolarized, $\varsigma = 0$, and fully polarized, $\varsigma = 1$, cases ($\varsigma = (n_\uparrow(\mathbf{r}) - n_\downarrow(\mathbf{r}))/n(\mathbf{r})$, where $n_\uparrow(\mathbf{r})$ and $n_\downarrow(\mathbf{r})$ represent the spin-up and spin-down densities, respectively), we found that the limit goes to zero for $0 \leq r_s \leq 10$. This range includes real system densities, as considered in the original PBE article,[3,24,25] Thus, when a PBE correlation-type functional is combined with VT{8,4}, Eq. (6) is satisfied for physical densities at least. In addition, this combination also has the advantage that the local spin density linear response of the homogeneous electron gas may be preserved for PBE.

The third correlation functional considered in this work is LYP.[4] When combined with various exchange functionals, LYP has proven capable of predicting a great variety of molecular properties. As already mentioned, Adamo and Barone[5] showed that E_{cLYP} in combination with the empirically parameterized Lacks-Gordon X-functional yields very good molecular energies and geometries. On the other hand, we have found numerically, also via a Mathematica procedure equivalent to the one described above for PBE, that the $\lim_{s\to\infty} s^{1/2} F_c(n,\ s)$ for the LYP correlation functional diverges, for $\varsigma = 0$ and for $\varsigma = 1$, for all values $0 \leq r_s \leq 10$. In the context of the VT{8,4} and VMT functional, it is also worth noting that, by construction and parameterization, E_{xLG} satisfies Eq. (8), yet its enhancement factor is very different from $F_{xVT\{8,4\}}$ or F_{xVMT}. For the noble gas systems on which it was tested, E_{xLG} also satisfies the LO bound. Inspection of the LG enhancement factor, which goes to very large values over a huge range of s, shows that LO satisfaction cannot be true in general. Since we are not studying F_{xLG} here, we leave that issue aside.

From our perspective, the combinations VT{8,4}-LYP and VMT-LYP are semi-empirical, in two specific senses. First, employment of LYP decouples the development of E_x and E_c. In contrast, as evidenced above, both $F_{xVT\{8,4\}}$ and F_{xVMT} were developed within the same context of constraints

as PBE and with PBE E_c in mind. Second, the LYP functional is based on an approximate wave-function which is known to be non-*N*-representable.[26] As used here, "semi-empirical" does not mean heavily parameterized to large sets of reference data ("training sets"). However, the parameters in LYP follow from the Colle-Salvetti[27] fit to Hartree-Fock data for the He atom, so LYP is not fully constraint-based. In any event, the popularity of the LYP functional makes studying the combinations with VT{8,4} (and VMT for thoroughness) virtually inescapable.

III. TEST SETS

For validation of the functionals presented here, we have followed conventional procedures. Specifically, we calculated standard enthalpies of formation of a large set of molecules, barriers heights for several chemical reactions, binding energies for weakly interacting systems, ionization potentials, electron affinities, proton affinities, bond lengths, and chemical shifts. In this section, we describe briefly the sets of systems used to calculate each of these properties. Note that in all cases the molecular geometries are recorded in the supplementary material (see Table S13).[28]

For the standard heat of formation ($\Delta_f H^0_{298}$), the test set was selected following the arguments of Staroverov *et al.*[29] The set consists of the 223 molecules in the G3/99 database.[30] Standard enthalpies of formation were calculated using the protocol described by Curtiss *et al.*[31] Geometries were optimized with the B3LYP[4,32–35] functional and the 6–31G(2*df*,*p*) basis set.[36] The harmonic frequencies were scaled by 0.9854. For all functionals reported, single-point calculations at those geometries were done with the Def2-TZVPP[37] basis set.

For the barrier heights we used the HTBH38/04 and NHTBH38/04 databases from Zhao and Truhlar.[38–40] Both sets consist of 38 transition state barrier heights corresponding to the forward and backward reactions of 19 hydrogen transfer reactions and 19 non-hydrogen transfer reactions. For each barrier, single-point calculations were done for the reactants (or products) and the transition states using QCISD/MG3 geometries that are available from the Truhlar group website.[41] The calculations were done with the Def2-TZVPP (Ref. 37 basis set).

The weakly interacting systems tested are the six hydrogen-bonded dimers in the HB6/04 database,[42] the seven charge-transfer complexes in the CT7/04 database,[42] the six dipole interaction complexes in the DI6/04 database,[42] the seven dispersion-interacting systems in the WI7/05 database,[38] and the five $\pi-\pi$ stacking complexes in the database PPS5/05.[38] This gives a total of 31 weakly interacting or non-bonded systems. The databases HB6/04, CT7/04, DI6/04, WI7/05, and PPS5/05 were developed in the Truhlar group and are available at their website.[41] The binding energies were evaluated by single-point calculations at the geometries available in those databases and using the 6–31++G(*d*,*p*) basis set.

The ionization potentials and electron affinities were calculated for the atoms and molecules in the IP13/3 (Refs. 43 and 44) and EA13/3 (Refs. 43 and 44) databases. In both cases, the molecular calculations were done adiabatically using the geometries from the Truhlar group database.[41] For the proton affinities, we selected the set designated as PA8 by Zhao and Truhlar,[45] based on the data from Parthiban and Martin,[46] which consists of eight small molecules. The geometries of the anions and neutral species necessary for the evaluation of the proton affinities are MP2(full)/6–31G(2*df*,*p*) optimized geometries that were taken from the Computational Thermochemistry database.[47] The chemical species involved in this test set belong to the G2/97 database.[31,48,49] Since the properties in this block are specially sensitive to the use of diffuse basis functions, the 6–31++G(*d*,*p*) basis set was used in the single-point calculations.

To test the structural capabilities of the GGA functional presented here, the bond lengths of the molecules in the test set T-96R, proposed by Staroverov *et al.*,[29] were calculated with the Def2-TZVPP (Ref. 37) basis set. The T-96R test set uses the experimental bond distances[50] of 96 molecules.

Finally, to validate the prediction of NMR data, we calculated the ^{13}C chemical shifts for the 14 small molecules with 17 geometrically different carbon atoms in a dataset originally proposed by Cheeseman *et al.*[51] We denote that set as NMR17/96. For the calculation of the chemical shifts, we used a 6–311++G(3*df*,3*pd*) orbital basis set with spherical Gaussians (5*d*/7*f*) and B3LYP/6–31G(*d*) optimized geometries that were taken from the NIST Computational Chemistry Comparison and Benchmark DataBase.[52]

IV. RESULTS AND DISCUSSION

The functionals VT{8,4} and VMT have been implemented in both the deMon2k (Ref. 53) and NWChem (Ref. 54) codes. Though the variational Coulomb fitting[55] used in deMon2k to eliminate four-center integrals is highly reliable, just to be conservative, all the data we present here are from NWChem, which computes such integrals explicitly. To have a reference, we also report the results for the non-empirical meta-GGA revTPSS,[56] obtained with the same methodology (NWChem).

The mean absolute deviations (MADs) for the properties included in the test sets described in Sec. III are reported in Tables II and III. From Table II, one can see that in 6 out of 10 properties, VT{8,4} is the functional with the smallest MADs among the GGAs tested in this work. In another three, VMT has the smallest MADs. However, PBEsol outperforms all the other GGAs in bond lengths. Interestingly, revTPSS is not always the exchange-correlation functional with the best performance. In fact, it has the smallest MADs in half of the properties reported in Table II. Another general feature that emerges from Table II (and that has been observed before) is that for energy differences, the functionals with μ_{GE} have larger MADS than their counterparts with μ_{PBE}. We now describe briefly the functional comparisons for each of the properties considered in the test sets.

Table II shows that for the standard heats of formation, the combination of VT{8,4} exchange and PBE correlation improves over the version with VMT exchange by about 5% in MAD, when one uses μ_{PBE}, and about 8% with μ_{GE}. The LYP correlation functional improves the performance of all the GGAs for this molecular property. Observe, for example,

TABLE II. Mean absolute deviations for the standard heats of formation (SHF), the barrier heights of the non-hydrogen transfer reactions, forward and reverse (NHBH-f/r), the barrier heights of the hydrogen transfer reactions, forward and reverse (HBH-f/r), the weakly interacting systems (WI), the ionization potentials (IP), electron affinities (EA), proton affinities (PA) and bond lengths (BL) of the test sets described in Sec. III. The X-functionals are PBE, the original VT{8,4}, and the prior VMT, plus their μ_{GE} analogs, PBEsol, VT{8,4}-GE, and VMT-GE. The C-functionals are the original PBE, PBE-GE, and LYP. For comparison, the results for the LG-LYP, and for calibration, the result from a meta-GGA revTPSS (with its own correlation functional), are also shown. See text regarding basis sets. All energies are in kcal/mol and distances are in Å.

Property	X	PBE	VT{8,4}	VMT	PBEsol	VT{8,4}-GE	VMT-GE	LG-LYP	revTPSS
	C	PBE	PBE	PBE	PBE-GE	PBE-GE	PBE-GE		
		LYP	LYP	LYP	LYP	LYP	LYP		
SHF		21.21	9.98	10.53	58.77	51.70	52.14	8.94	4.55
		12.06	7.79	7.56	42.49	35.48	35.91		
NHBH-f		10.38	9.79	9.82	11.88	11.50	11.53	11.17	11.18
		11.60	11.02	11.05	12.32	11.95	11.97		
NHBH-r		9.96	9.46	9.49	10.87	10.55	10.57	11.00	11.08
		11.02	10.53	10.55	11.45	11.14	11.16		
HBH-f		9.49	8.23	8.31	13.11	12.39	12.43	7.84	6.63
		9.68	8.42	8.50	12.77	12.06	12.10		
HBH-r		9.72	8.59	8.66	12.80	12.13	12.17	8.08	7.72
		9.70	8.58	8.64	12.48	11.82	11.86		
WI		1.64	1.53	1.52	2.29	2.06	2.07	1.80	1.41
		1.89	1.68	1.68	2.36	2.11	2.12		
IP		3.47	3.25	3.26	3.22	2.98	3.00	5.08	3.06
		4.22	4.14	4.14	4.36	4.48	4.46		
EA		2.64	2.48	2.48	3.24	3.01	3.03	4.15	2.45
		3.27	3.04	3.06	2.89	3.10	3.08		
PA		1.39	1.09	1.07	2.85	2.52	2.54	2.76	1.80
		2.82	2.32	2.34	4.60	4.17	4.19		
BL		0.0179	0.0211	0.0208	0.0144	0.0155	0.0154	0.0280	0.0204
		0.0235	0.0257	0.0255	0.0189	0.0196	0.0196		

the considerable decrease in the MAD of PBE exchange when it is combined with LYP correlation (43% smaller MAD than for PBE-PBE). From this table, one can conclude that, with a marginal difference, VMT and VT{8,4} exchanges combined with LYP are the best non-empirical GGAs to calculate standard heats of formation, with an important improvement over LG. In fact, they are off by about 3.1 kcal/mol or a 68% error relative to the next rung of complexity in the Jacob's ladder[57] of functionals, the revTPSS meta-GGA. Contrast this with the 7.5 kcal/mole or 165% relative error for PBE-LYP XC compared with revTPSS. However, these functionals are outperformed by OLYP, i.e., the combination of the empirical OPTX exchange of Handy and Cohen[58] and the LYP (Ref. 4) correlation functional. For the G3 set, OLYP has a MAD of 5.51 kcal/mol, a very acceptable value when compared with that of revTPSS. The individual deviations for each molecule can be found in Tables S1 and S2 of the supplementary material.[28]

For the non-Hydrogen reactions, in both directions (forward and reverse), the deviations are very similar, with an average MAD of 10.9 kcal/mol. Note that the functionals do not always respect the hierarchy of accuracy presumed in the Jacob's ladder. The revTPSS meta-GGA is worse than the μ_{PBE} GGAs for the non-Hydrogen cases but better than them for the Hydrogen-transfer cases. For non-Hydrogen reactions, VT{8,4} yields the smallest MAD, independent of the correlation functional, but only by a trivially small margin compared with VMT. For Hydrogen-transfer reactions, the hierarchy suggested in Jacobs's ladder is satisfied: for both reactions, revTPSS is the functional with the smallest MAD. However, in this case LG-LYP yields the best results among the GGAs. Interestingly, the average MAD (10.4 kcal/mol) is very close to that for the non-Hydrogen transfer reactions.

TABLE III. ^{13}C chemical shifts MADs (ppm) for the set of molecules used in Ref. 51. See text regarding basis sets. The B3LYP value is taken from Ref. 51.

X			PBE	VT{8,4}	VMT	VT{8,4}	VMT	B3
C	LSDA	PW91	PBE	PBE	PBE	LYP	LYP	LYP
	9.83	3.71	3.48	2.85	2.88	4.24	4.28	3.51

In all cases, the VT{8,4} exchange has slightly smaller deviations than VMT, indicating that the large-*s* constraint has some impact in these energy differences. Observe also that, in the majority of these cases, use of the LYP functional worsens matters, an indication that for some properties it may not be the best choice for the correlation contribution. Detailed results for each reaction for the cases of VT{8,4} or VMT X combined with the PBE and LYP functionals are in Tables S3–S6 of the supplemental material.[28]

Turning to the weakly interacting systems, one can note that the use of LYP correlation worsens the errors a little, although VT{8,4} and VMT provide slightly better results than PBE and LG. Among the functionals tested with this set, the meta-GGA (revTPSS) performs the best, in compliance with the Jacob's ladder hierarchy. A cautionary note is in order. The seemingly small values for the MADs in Table II should not be taken as indicative of acceptable performance of any of these functionals. For perspective, the reported MADs represent 40% (revTPSS) to 65% (PBEsol-cLYP) of the average interaction energies. Thus, none of these functionals is well suited to describe this kind of weakly interacting system.

For the one-electron processes, ionization potential and electron affinity, again with the exception of the PBEsol results for the electron affinity, the use of LYP degrades the prediction of these properties. Since the functionals tested do not correct the self-interaction error properly, have wrong asymptotic behavior, and do not have proper derivative discontinuity with respect to the total number of electrons, it is unsurprising that, for a given correlation functional, all the exchange functionals have very similar deviations from the experimental values. Thus, it is to be noted that for a given μ, VT{8,4} and VMT have almost the same MADs. Those, in turn, are very close to the corresponding PBE value. This behavior supports the expectation that the large-*s* behavior of the enhancement function is not the crucial factor for improving the prediction of these one-electron processes.

In contrast to the previous properties, the proton affinities are more sensitive to the large-*s* behavior of F_X. As can be seen in Table II, independently of the value of μ and the correlation used, the VMT and VT{8,4} functionals have a smaller MAD (between 0.3 and 0.5 kcal/mol) than that corresponding to PBE.

For the mean absolute deviations of the bond lengths reported in Table II, VT{8,4} and VMT are modestly worse than PBE or PBEsol, for both μ values. For the μ_{PBE} case, VT{8,4} and VMT errors are on par with revTPSS performance. Similarly to the several other cases already discussed, the use of LYP as the correlation functional increases slightly the error in the predicted bond distances, with the largest worsening in MAD being for PBE X, 0.0056 Å. Also in this case, VT{8,4} and VMT provide slightly better results than PBE and LG. On the other hand, in contrast with the energetic tests, the bond distances are described better with μ_{GE}, in keeping with the development of PBEsol. The shift in going from μ_{PBE} to μ_{GE} is not dramatic (the largest difference, 0.0056Å, occurs for VT{8,4}) but the result is that all three μ_{GE} GGAs do better than revTPSS.

Finally, the MADs for the ^{13}C chemical shifts are reported in Table III. From it one sees that, for the test set considered, VT{8,4}-PBE has the best performance. It may be worth noting that the MADs for PBE, VMT, and VT{8,4} decrease in that order, which is also the order shown by the large-*s* asymptote of the X enhancement functions of these functional.

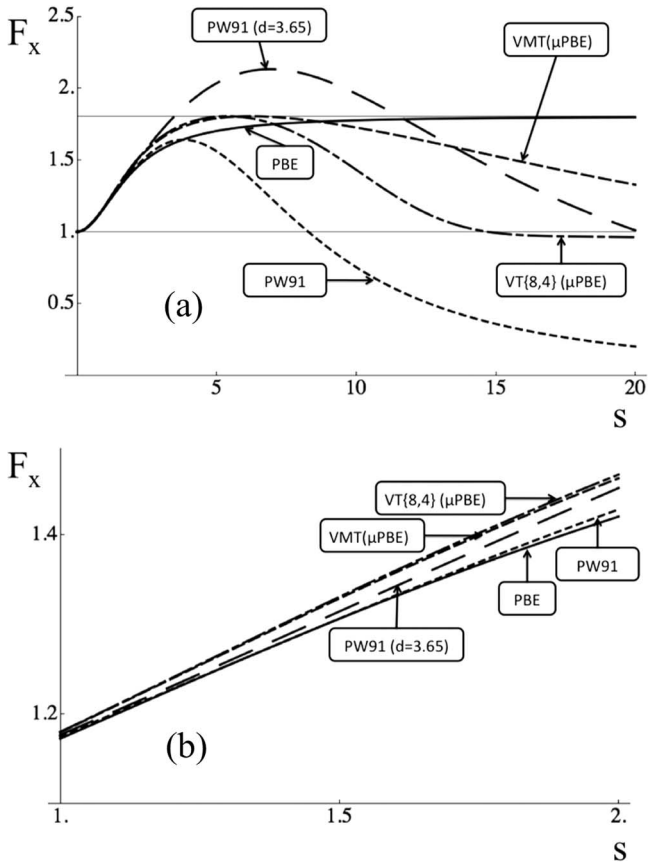

FIG. 2. Enhancement functions of several exchange functionals, (a) in the region $0 \leq s \leq 20$, and (b) in an enlargement of the small-*s* region to show the effect of imposing the non-uniform scaling constraint.

In the evaluation of properties such as atomization energies or formation enthalpies, the *s*-region that contributes most substantially to the exchange energy generally is thought to be $0 \leq s \leq 3$,[15,16,24,25] and thus, one cannot necessarily impute the trends in MADs directly to the large-*s* exchange enhancement function. To emphasize this point, in Figure 2(a) one can see that the very different asymptotic behaviors of the enhancement factors depicted do not correspond well with their comparative performance. PBE and PW91 have absolute deviations in formation enthalpies which are almost twice as big as those obtained with VT{8,4} or VMT. If the large-*s* behavior were a truly crucial ingredient, one would expect a very different MAD between PBE and PW91, and between VT{8,4} and VMT, behavior which disagrees with the observed MADs. Inspection of Figure 2(b), which is a magnified view of the small-*s* region, sheds some light on the observed performance. Notice that in this region, VT{8,4} and VMT run very close to each other and that PBE and PW91 do the same but, clearly, for $s \geq 1$, the first pair is distinguishable from the second. Enforcement or lack of enforcement of the asymptotic constraint manifestly has had an influence on the small-*s* behavior of the enhancement factors.

To strengthen this analysis, the large dashed curve in Figure 2 corresponds to a modified PW91 enhancement function for which the exponent of the term included to satisfy the non-uniform scaling has been reduced from $d = 4$ (using the same notation as Adamo and Barone[59]) to $d = 3.65$. As found originally by Adamo and Barone,[59] such a small change produces a dramatic effect in the modified PW91 X enhancement function. First, the maximum goes beyond the local-LO bound and the enhancement factor peak is at about $s \approx 7$ instead of $s \approx 4$ for PW91. But, Figure 2(b) shows that in the interval $1 \leq s \leq 2$, this modified PW91 exchange enhancement factor goes between the two behaviors described above for the two pairs of functionals. Indeed, the MAD obtained for the standard heats of formation of the G3 set with this modified PW91 is 12.44 kcal/mol, which is also in between the MADs of the two pairs. Thus, we confirm that the enforcement of the large-s constraint in VT{8,4} affects also the behavior of the enhancement function in the small-s region. It is that region which contributes predominantly to the evaluation of properties such as atomization energies and heats of formation of ordinary molecules. We, therefore, conclude that subtle improvements in behavior of the X enhancement functional in that region are significant for better GGA global performance.

V. CONCLUSIONS

We have presented a non-empirical GGA exchange functional, VT{8,4}, which is a modification of the recently proposed VMT functional that satisfies an additional constraint, namely, the large-s constraint, and evaluated its performance against a wide range of databases. The satisfaction of the large-s constraint demands an asymptotic decay of the exchange enhancement function to zero, and not to unity (the uniform electron gas value) as was enforced in VMT. The results for all the test sets considered, including standard enthalpies of formation, barrier heights for several chemical reactions, binding energies for weakly interacting systems, ionization potentials, electron affinities, proton affinities, bond lengths, and chemical shifts, indicate that the very different behaviors of the PBE, VMT, and VT{8,4} enhancement functions in the large-s region are not the main reason to explain the performance of these exchange functionals. Instead, we find that imposition of the large-s constraint induces subtle but important changes on the exchange enhancement function in the small-s region. Those changes seem to be responsible for the improved prediction of properties such as standard heats of formation. At the expense of losing its non-empirical nature, we have shown that the combination of VMT, VT{8,4}, or even PBE X with the LYP correlation functional improves the prediction of standard heats of formation considerably, while all the other properties are affected marginally. Due to the simple forms studied, the present work motivates the search for even better GGA exchange functionals and new constraints that will allow ease of implementation in any quantum chemical code, maintaining its speed but improving its overall performance, particularly, for Born-Oppenheimer surfaces for MD and for the prediction of NMR parameters (chemical shifts and spin-spin couplings). Such progress would enable applicability in very large systems (proteins, natural products, etc.) to predict the structure in solution of these highly important molecules.

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