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A new meta-GGA exchange functional based on an improved constraint-based GGA

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ABSTRACT

We report the performance of a non-empirical meta-GGA that comes from converting our simple VT{8,4} GGA. That GGA satisfies the large dimensionless reduced gradient limit, obeys the Lieb–Oxford bound, and reduces to the exact second-order gradient expansion approximation in the slowly varying limit. Validation studies of meta-VT{8,4} for several properties using well-known test sets shows a modest improvement with respect to revTPSS. Compared with the heavily parameterized M06-L, the heats of formation of meta-VT{8,4} are substantially better but reaction barrier heights are considerably worse. This suggests the opportunity for additional constraints and the need for better correlation functionals.

1. Introduction

Kohn–Sham (KS) density functional theory [1] provides an exact and, in principle, simple theoretical framework to incorporate exchange and correlation (XC) effects in the description of a many-electron system. Even with the limitations of contemporary approximations for the XC functional, KS–DFT is the most widely used method for electronic structure studies in quantum chemistry and solid state physics [2–6].

The different XC approximations sometimes are classified as local, semi-local and non-local. If well-constructed, the latter should provide, in general, a more accurate description of molecular and extended system structure and properties, at the expense of a greater computational effort than the first two. In terms of the Perdew–Schmidt [7] ‘Jacob's ladder’, the local spin density approximation (LSDA) corresponds to the first rung, the semi-local approximations comprise the second and third rungs, and the non-local approximations define the fourth and fifth rungs. In the first rung the XC functional depends solely upon the electronic density. The second rung corresponds to generalized gradient approximations (GGA) that incorporate the electron density gradient. Third rung functionals include the Laplacian of the density and/or the KS kinetic energy density. Fourth rung approximations incorporate a fraction or the full exact exchange, while fifth rung functionals introduce a dependence on the KS virtual orbitals. Note that although one expects accuracy to increase as one climbs the ladder, the accuracy achievable in principle within a given rung may not be achieved by published functionals.

The different approximations also may be classified as semi-empirical and non-empirical, depending on the way parameter values are fixed [6]. In the semi-empirical approach one fixes the parameters through the use of experimental or computed data, while in the non-empirical one, all parameters are fixed from mathematical and physical requirements, an approach sometimes called constraint satisfaction or constraint-based.

Recent development of approximate XC functionals has focused, to a great extent, on use of the information in the KS orbitals. Both the KS kinetic energy density and the Laplacian of the density have been used as ingredients to sharpen the sensitivity of the functional to localization versus delocalization and to the nuclear cusp behavior of the density [8–13]. The large incremental computational cost of using the next level of orbital information, exact exchange (either full or partial), means that it remains important to seek improvements on lower rungs of the Jacob's ladder. One route toward such improvement is the conversion of a good GGA functional to a meta-generalized GGA. The conversion procedure is well-documented and understood [8–13].

Not long ago, two of us and a co-author introduced a simple, constraint-based (non-empirical) GGA X functional, VMT [14]. In combination with the PBE correlation functional [15], VMT gives substantially better heats of formation than PBE XC at the cost of relatively low increase of mean-absolute errors in the bond lengths. More recently, a modified version of VMT, called VT{8,4}, was derived [16]. It respects an additional constraint upon the behavior of the XC energy density for large values of the reduced density gradient. Imposition of that constraint leads to a modest

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improvement over VMT. Based on that success, we present here the derivation of the meta-GGA based on VT{8,4} and assess its performance.

2. Meta-GGA exchange conversion summary

A GGA X functional may be expressed through the enhancement factor, $F_X(s)$, with respect to the local density approximation (LDA), for the spin-unpolarized case, in the form,

$$E_x[\rho] = \int d\mathbf{r}\rho(\mathbf{r})\varepsilon_{xLDA}[\rho(\mathbf{r})]F_x(s) \tag{1}$$

where $\varepsilon_{xLDA}[\rho(\mathbf{r})] = -(3/4)(3/\pi)^{1/3}\rho^{1/3}(\mathbf{r})$ and $s(\mathbf{r}) = |\nabla\rho(\mathbf{r})|/[2(3\pi^2)^{1/3}\rho^{4/3}(\mathbf{r})]$ is the reduced density gradient.

For context, the PBE GGA enhancement factor is [15]

$$F_X^{PBE}(s) = 1 + \kappa - \frac{\kappa}{1 + \frac{\mu s^2}{\kappa}} \tag{2}$$

where $\kappa = 0.804$ and $\mu = 0.21951$ are constants (unless noted otherwise, we use hartree atomic units). Parameters in the PBE functional are fixed through constraint satisfaction. The constant κ is related to the satisfaction of the local Lieb–Oxford bound [17,18], while the constant μ is related to the second-order term of the gradient expansion in the slowly varying limit. In the original PBE, the value of $\mu = 0.21951$ was set to cancel the second-order term of the correlation gradient expansion [19], in order to recover the LDA linear response. Later [20], a different parameterization of the PBE exchange energy was proposed with $\mu = \mu_{\rm GEA} = 10/81 \approx 0.12346$, the value in the exchange second-order gradient expansion approximation (GEA) [21]. This parameterization, PBEsol, was found to be more appropriate for the description of lattice constants.

The PBE enhancement function is the basis for the meta-GGA exchange functionals PKZB [8], TPSS [9] and revTPSS [13]. Among those three functionals, revTPSS leads to the best description of molecular properties, particularly the heats of formation. Thus, in the present work we use the revTPSS procedure for the derivation of the meta-GGA based on VT{8,4}. The procedure is to replace the product μs^2 in the enhancement function, e.g. Eq. (2), by a new variable x. In turn, x is written in terms of variables p, z, and q_b. The first two are defined as $p = s^2$ and $z = \tau^W/\tau \leqslant 1$. Here τ is the kinetic energy density of the occupied Kohn–Sham orbitals $\phi_i(\mathbf{r})$,

$$\tau(\mathbf{r}) = \frac{1}{2}\sum_i^{occ}|\nabla\phi_i(\mathbf{r})|^2 \tag{3}$$

and $\tau^W(\mathbf{r}) = |\nabla\rho(\mathbf{r})|^2/8\rho(\mathbf{r})$ is the von Weizsäcker kinetic energy density. The remaining definition is

$$q_b = (9/20)(\alpha - 1)/[1 + b\alpha(\alpha - 1)]^{1/2} + 2p/3 \tag{4}$$

where

$$\alpha = (\tau - \tau^W)/\tau^{\rm unif} = (5p/3)(z^{-1} - 1) \geqslant 0 \tag{5}$$

and $\tau^{\rm unif} = \frac{3}{10}(3\pi^2)^{2/3}\rho^{5/3}$ is the uniform-gas kinetic energy density. The quantity q_b tends to the reduced Laplacian $q = \nabla^2\rho/[4(3\pi^2)^{2/3}\rho^{5/3}]$ in the slowly varying limit. For one- and two-electron densities $\tau = \tau^W$, $z = 1$ and $\alpha = 0$, while for a slowly varying density, $z \approx 5p/3$ and $\alpha \approx 1$. In the notation of Refs. [9,13], the new variable x contains three parameters b, c, and e.

The form given to x allows one to recover the gradient expansion up to sixth order. The parameter b is equal to 0.40, and the parameters c and e are fixed by requiring the exchange potential at the nucleus to be finite for one- and two-electron ground state densities, and to yield the exact value, −0.3125 hartree, for the exchange energy corresponding to the exact ground-state density of the hydrogen atom. Thus, this meta-GGA procedure introduces important constraints related to both the uniform electron gas and to one- and two-electron systems.

The VT{8,4} GGA X enhancement factor is [16]

$$F_x^{VT\{8,4\}}(s) = 1 + \frac{\mu s^2 e^{-\gamma s^2}}{1 + \mu s^2} + (1 - e^{-\gamma s^4})(s^{-2} - 1), \tag{6}$$

where μ may be set either to the original PBE value, $\mu_{\rm PBE} = 0.21951$, or to the GEA value, $\mu_{\rm GEA} = 10/81 \approx 0.12346$. The parameter γ is fixed through local imposition of the Lieb-Oxford bound (LO), $F_x^{VT\{8,4\}}(s) \leq \lambda_{LO}$, such that the equality occurs at the maximum value of the enhancement function for the chosen value of μ. Thus, one finds that for $\mu_{\rm PBE} = 0.21951$, $\gamma = 0.000074$, and for $\mu_{\rm GEA} = 10/81 \approx 0.12346$, $\gamma = 0.000023$. The third term in Eq. (6) corresponds to the correction to VMT X (the sum of the first two terms) required to fulfill the relevant asymptotic requirement,

$$\lim_{s\to\infty} s^{1/2}F_x(s) < \infty \tag{7}$$

Thus, using Eq. (6) for the meta-VT{8,4} one has

$$F_x^{{\rm meta}-VT\{8,4\}}(x) = 1 + \frac{xe^{-\frac{\gamma}{\mu}x}}{1 + x} + \left(1 - e^{-\gamma\left(\frac{x}{\mu}\right)^2}\right)\left(\frac{\mu}{x} - 1\right) \tag{8}$$

where

$$x = \left\{\left[\frac{10}{81} + c\frac{z^3}{(1 + z^2)^2}\right]p + \frac{146}{2025}q_b^2 - \frac{73}{405}q_b\sqrt{\frac{1}{2}\left(\frac{3}{5}z\right)^2 + \frac{1}{2}p^2} + \left(\frac{\gamma}{\mu^2} + \frac{\gamma}{\mu} + 1\right)\left(\frac{10}{81}\right)^2 p^2 + 2\sqrt{e}\frac{10}{81}\left(\frac{3}{5}z\right)^2 + e\mu p^3\right\}\Big/(1 + \sqrt{e}p)^2, \tag{9}$$

Note that x in this equation is slightly different from x in Ref. [13], in order to recover the gradient expansion up to but not including sixth order. On the other hand, following the criteria used in TPSS, one finds that $c = 2.14951$ and $e = 1.987$, while the value of the parameter b is kept equal to 0.40.

For large-p the variable $x \to \mu p$, so that the enhancement function of the meta-GGA becomes equal to that of the corresponding GGA. This situation was used in TPSS to set the value of μ to that of the original PBE, that is, $\mu = 0.21951$. However, in revTPSS the value of μ was changed towards the PBEsol value (GEA, $10/81 = 0.12346$) by choosing $\mu = 0.14$. In meta-VT{8,4}, we have chosen to constrain μ to the GEA value.

Additionally, one can see from Eq. (2) that neither PBE nor revTPSS (which becomes identical to PBE when $p \to \infty$) satisfies the constraint given by Eq. (7). However, since VT{8,4} was built to satisfy it, meta-VT{8,4} also satisfies it, because meta-VT{8,4} becomes identical to VT{8,4} as $p \to \infty$. In Table 1 we report the values of the parameters μ, c, and e for the different TPSS-type functionals.

Figures 1 and 2 show the behavior of the revTPSS and meta-VT{8,4} enhancement functions for $\alpha = 0$, which describes one- and two-electron systems (Figure 1), and for $\alpha = 1$, which describes, for small s values, the slowly varying regime (Figure 2). Both figures show that in the physically important region $0 < s < 3$ the two functions have practically the same behavior. In

Table 1
Parameters for the meta-GGA exchange functionals considered in this work.

Functional	μ	c	e
TPSS	$\mu_{\rm PBE}$	1.59096	1.537
revTPSS	0.14	2.35204	2.168
meta-VT{8,4}	$\mu_{\rm GEA}$	2.14951	1.987

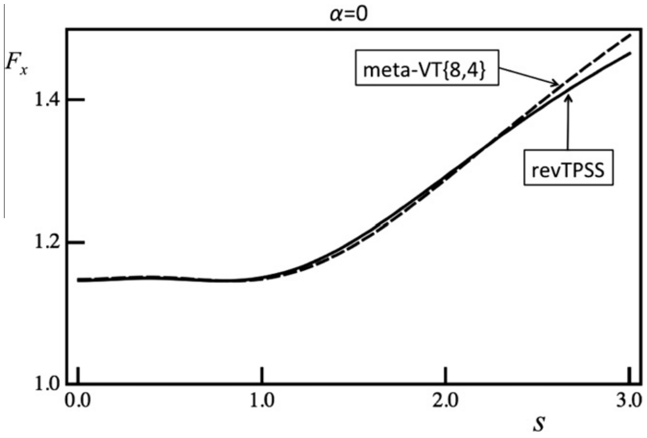

Figure 1. Exchange enhancement factor as a function of the reduced density gradient for revTPSS and meta-VT{8,4} for $\alpha = 0$, which corresponds to ground-state densities of one- and two-electron systems.

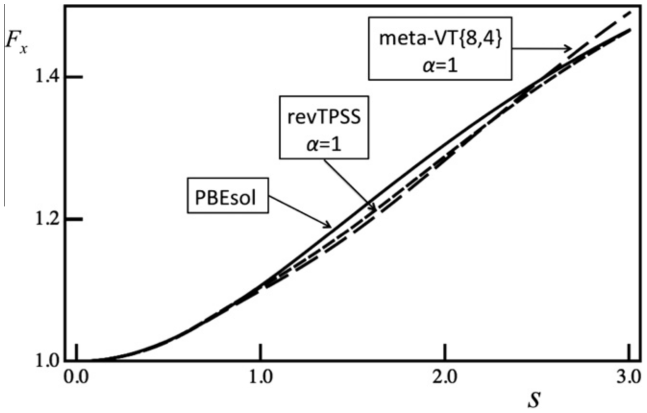

Figure 2. Exchange enhancement factor as a function of the reduced density gradient for PBEsol and for revTPSS and meta-VT{8,4} for $\alpha = 1$. The slowly varying limit corresponds to $\alpha \approx 1$ and $s \approx 0$.

Figure 2 we have also included PBEsol, to show that it lies very close to meta-VT{8,4} and to revTPSS for $s < 1$, because all of them reduce to the second-order GEA in this region.

The meta-VT{8,4} exchange energy functional may be combined with the revTPSS correlation energy [13]. The latter has important improvements over the GGA correlation of PBE. Among other features, the revTPSS C functional vanishes for one-electron systems, as it should.

3. Results and discussion

To assess the performance of the non-empirical meta-VT{8,4} exchange energy functional developed here, we have first determined the exchange energy of atoms H through Ar for several GGA and meta-GGA functionals, by carrying out exchange-only calculations with a Def2–QZVP basis set [22] in a developmental version of NWChem vers. 6.0 [23]. The results are presented in Table 2, where the Hartree–Fock values for the same basis set are included and used to determine the mean absolute error (MAE) of each functional. One can see that B88 [24] meets this particular test best. However, it is essential to recognize that the B88 functional has one parameter whose value was determined by a least squares fit to the Hartree–Fock exchange energies of the six noble gas atoms He–Rn. Thus, B88 provides an indication of possible attainments of other non-empirical functionals. In this context, one can see that VT{8,4} and meta-VT{8,4}, both of which satisfy the large reduced density gradient limit, lead to a better description of the exchange energies than PBE, and a slightly worse description than revTPSS. Another important aspect, is that the results for the exchange energy of the non-empirical revTPSS and the meta-VT{8,4}, are rather similar to those obtained through the semi-empirical meta-GGA, M06-L [25], which is heavily parameterized (as will be described below) for other properties.

We have also done studies for atoms and molecules following the customary practice of determining the MAEs associated with the results obtained for test sets assembled for specific properties.

For comparison purposes, the same studies were carried out for the meta-GGA functionals TPSS, revTPSS, and M06-L. Additionally, we also report the results for two hybrids, the non-empirical PBEmolβ0 [26] and the semi-empirical B3LYP [24,27–30]. Since the hybrids belong to the fourth rung of Jacob's ladder, they provide a reference for any improvements achieved at the third rung.

We have done calculations, for the test sets indicated in parentheses, of standard heats of formation (G3/99 [31] with 223 molecules), ionization potentials and electron affinities (IP13/3 [32] and EA13/3 [33] with six atoms and seven molecules), proton affinities (PA8 [34,35] with eight molecules), binding energies of weakly interacting systems (HB6/04 [36], CT7/04 [36], DI6/04 [36], WI7/05 [37], and PPS5/05 [37] with a total of 31 systems), barrier heights for hydrogen (HTBH38/04 [37–40] with 38 cases) and non-hydrogen (NHTBH38/04 [37–40] with 38 cases) transfer reactions, bond distances (T-96R [41] with 96 molecules) and harmonic frequencies (T-82F [41] with 82 molecules).

For the determination of the standard heats of formation we followed the procedure described in Ref. [42]. In the case of the ionization potentials and the electron affinities, the molecular calculations were done adiabatically, with the geometries reported in Ref. [38]. The proton affinities were computed using the geometries of the anions and neutral species from MP2(full)/6-31G(2df,p) calculations as reported in Ref. [43]. The basis set 6-31++G(d,p) was used for the ionization potentials, electron affinities, proton affinities, and binding energies of weakly interacting systems, while for the other properties the basis set Def2–TZVPP [22] was used. All the calculations were done with the same developmental version of NWChem as was used for the atomic exchange energies.

It is important to note that M06-L is a semi-empirical functional that contains 37 parameters [25], whose values are fixed, among other conditions, by minimizing the MAE in the test sets for ionization potentials, electron affinities, proton affinities, binding energies of weakly interacting systems, and the barrier heights for hydrogen and non-hydrogen transfer reactions that we are considering, together with a test set for atomization energies and various other test sets for other properties. Thus, it also provides a reference, like the hybrids, for the performance of the non-empirical meta-GGA functionals considered in the present work.

The results are reported in Table 3, where one can see that the performance of meta-VT{8,4} is comparable to that of revTPSS but usually mildly superior, for all properties. From the perspective of constraint satisfaction, meta-VT{8,4} satisfies more constraints. It satisfies the large s limit given by Eq. (7) and the GGA embedded in it reduces to the exact second-order GEA in the slowly varying limit. If one carries out revTPSS calculations with μ set equal to the second-order GEA value, 10/81 (for which $c = 2.58589$ and $e = 2.363$), one finds that the MAE for the heats of formation is equal to 6.18 kcal/mol, that is, it deteriorates by slightly more than 1.5 kcal/mol (38%). Also, it is noteworthy that metaVT{8,4} and revTPSS both lead to a better description of the heats of formation than the semi-empirical M06-L by more than 1 kcal/mol (20%) in MAE. The need for further improvement of constraint-based

Table 2
Exchange energies and mean absolute errors (MAE) with respect to the Hartree–Fock values, in hartrees, as determined by exchange-only calculations using three GGA and three meta-GGA functionals.

Atom	Exchange energy						
	Hartree–Fock	B88	PBE	VT{8,4}	revTPSS	Meta-VT{8,4}	M06-L
H	−0.313	−0.306	−0.301	−0.304	−0.311	−0.311	−0.318
He	−1.026	−1.016	−1.002	−1.011	−1.025	−1.026	−1.040
Li	−1.781	−1.768	−1.748	−1.762	−1.783	−1.782	−1.802
Be	−2.667	−2.652	−2.627	−2.647	−2.671	−2.669	−2.667
B	−3.770	−3.748	−3.716	−3.740	−3.775	−3.771	−3.769
C	−5.077	−5.048	−5.008	−5.036	−5.065	−5.060	−5.065
N	−6.607	−6.569	−6.521	−6.551	−6.578	−6.572	−6.587
O	−8.218	−8.188	−8.131	−8.165	−8.198	−8.190	−8.199
F	−10.045	−10.021	−9.954	−9.990	−10.012	−10.001	−10.019
Ne	−12.108	−12.087	−12.009	−12.047	−12.060	−12.048	−12.072
Na	−14.017	−13.977	−13.891	−13.933	−13.944	−13.929	−13.960
Mg	−15.994	−15.954	−15.863	−15.908	−15.907	−15.889	−15.901
Al	−18.092	−18.055	−17.952	−18.000	−17.992	−17.972	−17.990
Si	−20.304	−20.261	−20.147	−20.198	−20.180	−20.158	−20.183
P	−22.642	−22.593	−22.467	−22.521	−22.493	−22.469	−22.509
S	−25.034	−24.976	−24.837	−24.893	−24.865	−24.840	−24.887
Cl	−27.544	−27.481	−27.329	−27.388	−27.349	−27.321	−27.376
Ar	−30.185	−30.119	−29.953	−30.015	−29.964	−29.935	−30.003
MAE		0.033	0.109	0.073	0.071	0.083	0.064

Table 3
Mean absolute errors (MAE) for several properties as calculated with four meta-GGA functionals and two hybrids. All energies are in kcal/mol, bond distances in Å, and frequencies in cm^{-1}.

Property	MAE					
	TPSS	revTPSS	meta-VT{8,4}	M06-L	PBEmolβ0	B3LYP
Heats of formation	5.31	4.55	4.35	5.66	5.65	5.69
Ionization potentials	3.27	3.06	3.00	3.62	5.33	4.76
Electron affinities	2.29	2.45	2.61	3.74	2.78	3.26
Proton affinities	1.66	1.80	1.90	1.40	1.11	1.31
Binding energies of weakly interacting systems	1.44	1.41	1.43	0.94	1.00	1.17
Reaction barrier heights						
Hydrogen transfer forward	7.53	6.63	6.44	3.28	3.26	4.29
Hydrogen transfer backward	8.37	7.72	7.52	5.17	4.13	4.65
Non-hydrogen transfer forward	11.18	11.18	11.04	6.00	6.66	7.81
Non-hydrogen transfer backward	9.92	10.08	9.99	5.72	6.00	6.67
Bond distances	0.0155	0.0204	0.0205	0.0086	0.0090	0.0108
Frequencies	31.75	39.58	39.32	45.32	41.80	35.23

metaGGAs is clear however: neither of the TPSS type functionals provides a good description of kinetic properties and bond distances in comparison with M06-L.

In fact, if one compares the results obtained for the heats of formation with those obtained using a hybrid functional, like the non-empirical PBEmolβ0 [26] or the semi-empirical B3LYP, one can see that revTPSS and meta-VT{8,4} are more than 1 kcal/mol lower in MAE. Once again, however, the comparative performance of these two meta-GGA functionals with respect to the barrier heights and the bond distances is rather poor.

4. Conclusions

The performance of the new non-empirical meta-GGA functional meta-VT{8,4} that comes from converting our simple VT{8,4} GGA is modestly better than revTPSS where that latter functional is good and about the same where that functional is poor. The new functional satisfies the constraint on the behavior of the enhancement function for large values of the reduced density gradient.

The comparison with the hybrids shows that the meta-GGA functionals lead to somewhat better description of the heats of formation, but to a poorer description of barrier heights and bond distances. Since the computational effort at the meta-GGA level is smaller than the one corresponding to the hybrid functionals, it seems worthwhile to work on improvement of the non-empirical meta-GGA functionals, to reach a precision in the prediction of kinetic and structural properties comparable to that of the hybrid functionals. The fact that the semi-empirical M06-L functional does lead to a rather good description of the barrier heights and the bond distances means that there must be a constraint-based functional that does equally well. Two obvious potential routes to progress are to use a better correlation functional and to find additional pertinent constraints. The analytical behavior of M06-L may be a clue to such developments.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cplett.2012.06.025.

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