THE JOURNAL OF CHEMICAL PHYSICS **130**, 244103 (2009)

Variable Lieb–Oxford bound satisfaction in a generalized gradient exchange-correlation functional

A. Vela,[1,a)] V. Medel,[1] and S. B. Trickey[2]
[1]*Departamento de Química, Cinvestav, Av. IPN 2508, Colonia San Pedro Zacatenco, Mexico Distrito Federal 07360, Mexico*
[2]*Department of Physics and Department of Chemistry, Quantum Theory Project, University of Florida, P.O. Box 118435, Gainesville, Florida 32611-8435, USA*

(Received 10 March 2009; accepted 20 May 2009; published online 24 June 2009)

We propose a different way to satisfy both gradient expansion limiting behavior and the Lieb–Oxford bound in a generalized gradient approximation exchange functional by extension of the Perdew–Burke–Ernzerhof (PBE) form. Motivation includes early and recent exploration of modified values for the gradient expansion coefficient in the PBE exchange-correlation functional (cf. the PBEsol functional) and earlier experience with a numerical cutoff for large-s ($s \propto |\nabla n|/n^{4/3}$) in a version of the deMon molecular code. For either the original PBE or the PBEsol choice of the gradient coefficient, we find improved performance from using an s-dependent (spatially varying) satisfaction of the Lieb–Oxford bound which quenches to uniform electron gas behavior at large s. The mean absolute deviations (MADs) in atomization energies for a widely used test set of 20 small molecules are reduced by about 22% relative to PBE and PBEsol. For these small molecules, the bond length MADs are essentially unchanged. © *2009 American Institute of Physics*.
[DOI: 10.1063/1.3152713]

I. BACKGROUND AND MOTIVATION

The Perdew–Burke–Ernzerhof[1] (PBE) generalized gradient approximation (GGA) exchange-correlation (XC) functional is arguably the most widely used GGA today. It is constraint based, that is, numerical values of parameters in the PBE functional are set solely by requiring satisfaction of exact constraints (limits, asymptotics, bounds, etc.). Since there are more constraints than can be satisfied by a relatively straightforward GGA form, an inescapable issue is which constraints to satisfy and which to give up. Closely related to such choices are issues of constraint implementation, e.g., pointwise versus global.

The exchange component of PBE is given in terms of an enhancement factor with respect to local exchange, to wit,

$$E_X[n] = \int d\mathbf{r}\, n(\mathbf{r})\varepsilon_{x\text{LDA}}[n(\mathbf{r})]F_{x\text{PBE}}[s(\mathbf{r})],$$

$$\varepsilon_{x\text{LDA}}[n(\mathbf{r})] := C_X n^{1/3}(\mathbf{r}), \tag{1}$$

$$C_X := -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3},$$

with

$$F_{x\text{PBE}}(s) := 1 + \kappa - \frac{\kappa}{1 + \mu s^2/\kappa}. \tag{2}$$

The dimensionless reduced gradient s is given by

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

The constants μ and κ are determined by appealing to relevant constraints. In the original PBE formulation, $\mu_{\text{PBE}} = 0.219\,51$ in order to obtain correct local spin density linear response in the limit $s \to 0$ by cancellation of the quadratic term (in that limit) from the PBE correlation functional. Recently, Csonka *et al.*[2] discussed diminishing the gradient dependence in terms of an approximate effective self-interaction correction. Shortly thereafter, Perdew *et al.*[3] gave the PBEsol modification of PBE E_{XC}. One of the two modifications in PBEsol is to reduce μ to the value appropriate for the second-order gradient expansion for exchange in the weakly inhomogeneous electron gas, $\mu_{\text{GE}} = 10/81$. The compromise introduced by this reduction is that atomization energies are worsened in PBEsol relative to those from PBE, but crystal lattice constants are improved.[3] The reasons why $\mu \approx 2\mu_{\text{GE}}$ is preferable for finite systems are discussed in Refs. 4 and 5.

In the PBE X functional, κ is set from the Lieb–Oxford (LO) bound[6] via appeal to the $s \to \infty$ limit of the fully spin-polarized system. In the density functional theory literature, the LO bound customarily is written as

$$\frac{E_{\text{XC}}[n]}{E_X^{\text{LDA}}[n]} \le \lambda_{\text{LO}},$$
$$E_X^{\text{LDA}}[n] = \int d\mathbf{r}\, n(\mathbf{r})\varepsilon_{x\text{LDA}}[n(\mathbf{r})]. \tag{4}$$

Notice that this is a global bound. The original LO value of the bounding constant is $\lambda_{\text{LO}} = 2.2733$. There has been recurring interest in making this bound tighter in connection with improved E_{XC} approximations. Indeed, Chan and Handy[7] found the slightly tighter value of $\lambda_{\text{CH}} = 2.2149$. In PBE, the

---

[a)] Electronic mail: avela@cinvestav.mx.

LO bound is enforced upon $F_{x\mathrm{PBE}}(s)$, hence is pointwise or local, a sufficient but not necessary condition.

Shortly after the PBE GGA appeared, a modification with a smaller value of κ was used to get better lattice constants,[8] but the detailed studies to rationalize the change were, at that point, unpublished. A bit later, a version called revPBE was introduced by Zhang and Yang.[9] For non-spin-polarized densities, revPBE is guaranteed to satisfy the LO bound locally but there is no such guarantee for spin-polarized densities. Subsequently, Hammer *et al.*[10] introduced a modification of PBE X called RPBE. It has an s-dependent form of local satisfaction of the LO bound in the enhancement factor,

$$F_{x\mathrm{RPBE}}(s) \coloneqq 1 + \kappa[1 - \exp(-\mu s^2/\kappa)]. \qquad (5)$$

In 2001 the numerical studies which rationalized the modifications in Ref. 8 appeared.[11] A general trend with a somewhat peculiar exception was found. For the $3d$ metals, the original κ value was needed to get the best lattice constants. For the $4d$ metals, a reduced value of ≈ 0.5 was better, and the $5ds$ needed an even lower value of ≈ 0.3. However, in the case of spin-polarized Fe, a large value of ≈ 1.0 was needed. Interestingly, this change did not affect the relative ordering of phases in Fe.

Recently, Odashima and Capelle[12] provided substantial numerical evidence from exact and near-exact calculations on atoms, small molecules, and model systems that the actual bound is much tighter, $\lambda_{\mathrm{OC2}}=2.0$ even when very diffuse systems are included. Excluding such systems, the value seems to be even smaller, about 1.35. Zhao and Truhlar[13] then combined the restoration of the gradient expansion coefficient with the reduced LO bound λ_{OC2} (Zhao and Truhlar actually used 1.9555). Their SOGGA modified functional is a half and half mixture of the PBE and RPBE exchange enhancement factors, each with μ_{GE}, and thereby is exact through second order in the X gradient expansion. The SOGGA functional improves on lattice parameter for 18 solids by 20% with respect to PBE but does not improve atomization energies relative to PBE for a small set of molecules.

Here we discuss the effects of using a spatially varying (i.e., s-dependent) implementation of the LO bound which differs significantly from both RPBE and SOGGA, with either the original value of the gradient coefficient μ_{PBE} or the diminished value μ_{GE} (see below). The primary distinction is that our new enhancement factor always is tighter than λ_{LO} or λ_{OC2} (except for one value of s, where it equals whichever of those constants are selected for constraining the functional). We show that the resulting functional, in combination with the unmodified PBE correlation energy functional, provides significant improvement over PBE and PBEsol, depending on which choice of gradient coefficient is used.

II. MODIFIED ENHANCEMENT FACTOR

On the basis of the findings just summarized, we elect to use either the value of $\mu_{\mathrm{GE}}=10/81=0.123\,457\ldots$ which is consistent with the gradient expansion for the weakly inhomogeneous electron gas or the original PBE value $\mu_{\mathrm{PBE}}=0.219\,51$. As an aside, we note that we have explored smaller μ values. Smaller values of μ can be rationalized by use of a screened interaction or by appeal to a quasiclassical analysis of E_X in the weakly inhomogeneous electron gas.[14,15] However, use of such values goes outside the framework of constraint-based development. Thus, we will report semiempirical versions of the present approach separately.[16]

Next, consider ways in which a tighter LO bound might occur in a modified PBE functional. To have the enhancement factor in Eq. (2) satisfy Eq. (4) for all possible densities is equivalent to

$$F_x[s] \le \frac{\lambda_{\mathrm{LO}}}{2^{1/3}} \approx 1.804. \qquad (6)$$

The $2^{1/3}$ factor comes from requiring that the bound be satisfied for fully spin-polarized systems. Then

$$\lim_{s\to\infty} F_x[s] = 1 + \kappa \Rightarrow \kappa_{\mathrm{PBE}} = 0.804. \qquad (7)$$

In an early version of what has evolved to be the deMon2k code,[17] a pragmatic cutoff prefactor[18] was introduced in both E_X and its functional derivative (the exchange potential v_X) for the PW86 GGA (Ref. 19) to gain numerical stability. The motivation was that the inhomogeneity variable s can be quite large in regions of small density: $\lim_{n\to 0} s \propto n^{-1/3}$. Upon examination,[20] it became clear that the effect of this cutoff was to make calculated molecular bond lengths somewhat better with respect to experiment than unaltered PW86 results. The cutoff form was

$$F_{\mathrm{cut}} = \exp\left(-\frac{h|\nabla n|^2}{n^{8/3}}\right), \qquad (8)$$

with $h=1\times10^{-4}$. This cutoff was an unintentional, *ad hoc* modification of the LO bound. The modification was inconsistent, since the same cutoff prefactor was used for both E_X and v_X.

From that experience, however, the thought arises that perhaps a consistent, constraint-based version of such a cutoff would give an improved E_X. There are straightforward physical reasons to support the idea as well. Densities decay piecewise exponentially[21,22] and generally are rather smooth. The numerical evidence[23] is that $0 \le s \le 3$ for the major part of most densities. Thus, there are few circumstances in which the density gradient itself is large. In many systems (notably, highly anisotropic ones), large s occurs in regions of small, smooth densities, not large density gradients, because of the aforementioned divergence. For such regions of small density gradients for small density, one therefore has the somewhat counterintuitive situation that large s corresponds to the weakly inhomogeneous electron gas, i.e., LDA. Therefore, an additional constraint is that for large but physically significant s, $F_x \to 1$. Obviously, PBE does not satisfy this constraint nor does the Zhao–Truhlar SOGGA X functional. Its large s behavior is just like PBE except for going to a lower constant, but not unity. In principle, one can only impose the new constraint if s is not too large because for $s\to\infty$ there is an exact asymptotic requirement,[24] namely, that

$$\lim_{s\to\infty} s^{1/2}F_{XC} < \infty, \tag{9}$$

which is violated if $F_x \to 1$ as $s\to\infty$. We return to this asymptotic behavior issue shortly. Even if the foregoing arguments are only suggestive, it remains true that the region $s \gg 1$ is poorly understood and approximations with different behaviors for this region merit further exploration.

Our objective therefore is an enhancement factor which will recover electron gas behavior both for large s and for $s\to 0$, recover the gradient expansion, and satisfy the LO bound for all s. Furthermore, it would be desirable to have a functional which relates smoothly, in the appropriate limits of any new parameters, to $F_{x\mathrm{PBE}}$ in the relevant range of s. Therefore, we propose the form

$$F_{x\mathrm{VMT1}} \coloneqq 1 + \frac{\mu s^2 \exp(-\alpha s^2)}{1+\mu s^2} \tag{10}$$

and choose either $\mu=\mu_{\mathrm{PBE}}$ or the gradient expansion value of $\mu=\mu_{\mathrm{GE}}=10/81$ on grounds just discussed. Note that this form is a small simplification of a form which gives $F_{x\mathrm{PBE}}$ in the limit $\alpha\to 0$, namely,

$$F_{x\mathrm{VMT2}} \coloneqq 1 + \frac{B\mu s^2 \exp(-\alpha s^2)}{B+\mu s^2},$$
$$B \coloneqq \kappa_{\mathrm{PBE}}(1-\alpha). \tag{11}$$

For simplicity, in this work we use the form in Eq. (10).

The proposed form, Eq. (10), also does not obey the asymptotic constraint equation (9). As just remarked, however, neither does the original PBE nor any of the subsequent PBE modifications discussed above. As frequently emphasized by Perdew *et al.* (at least as far back as Ref. 1), no simple GGA form can satisfy all the known constraints for E_X. Our choice is to employ a significantly tightened, spatially LO bound for large but finite s and give up on the asymptotic constraint in s, Eq. (9).

For Eq. (10), the remaining calibration is to choose α such that the specified LO bound (e.g., λ_{LO} or λ_{OC2}) is satisfied, as follows. For each value of α and μ and for $s\geq 0$, the region of physical interest, the proposed enhancement function, Eq. (10), has a single maximum, located at

$$s_{\max}(\alpha,\mu) = \left[\frac{1}{2\mu}\left(\sqrt{\frac{4\mu}{\alpha}+1}-1\right)\right]^{1/2}. \tag{12}$$

As seen in Fig. 1, $s_{\max}$ is a smooth and well-behaved function of both μ and α. Then, the LO bound is satisfied if

$$F_{x\mathrm{VMT1}}(s_{\max}) = \frac{\lambda_\infty}{2^{1/3}}, \tag{13}$$

with λ_∞ equal either to λ_{LO} or λ_{OC2}. Again, to stay within the regime of strict constraints, we consider only λ_{LO} in this study. The resulting values of α and $s_{\max}$ are summarized in Table I. Figure 2 shows the relationship between values of μ, hence of α, and satisfaction of the LO bound. At all but one value of s, the effective bound is tightened.

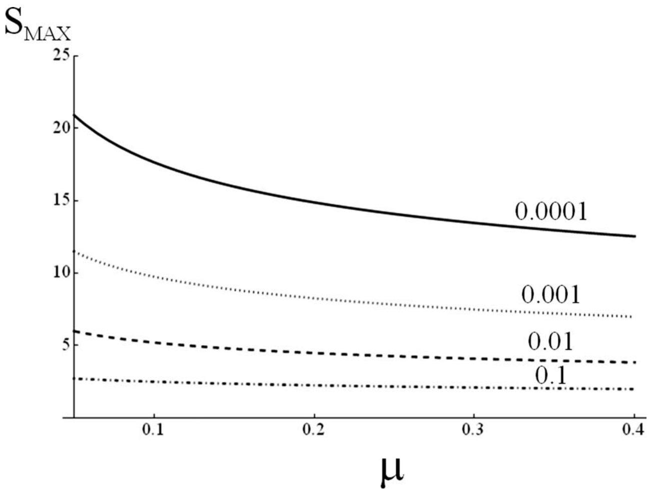

FIG. 1. Behavior of $s_{\max}$ as a function of μ for a large range of α values.

III. RESULTS AND DISCUSSION

For testing, we have used the same set of 20 light molecules (H_2, LiH, OH, H_2O, HF, Li_2, LiF, Be_2, CO, N_2, O_2, F_2, P_2, NO, NH_3, Cl_2, C_2H_2, C_2H_4, CH_4, and HCN) as in Ref. 25. The calculations were done with the deMon2k code[17] modified to incorporate the new functional. For high-quality geometry optimization, we used the DZ-ANO (Ref. 26) orbital basis set which is available in deMon2k. The auxiliary basis set for the variational Coulomb fitting was the automatically generated GEN-A2* set that consists of spdfg Hermite Gaussian functions.[27] Exchange-correlation quantities were evaluated on the numerical integration grid directly from the fitted (auxiliary) density ("AUXIS" option in deMon2k),[28] and the grid used for the integration is the default adaptive grid available in deMon2k.[29]

For brevity, we report results corresponding to the exchange enhancement function of Eq. (10) as VMT. Tables II–IV give the total energies, atomization energies, and geometric parameters, respectively. Table V and Fig. 3 summarize these results in terms of mean absolute deviations (MADs) relative to experiment. For clarity of comparison, we have used the experimental values given in Table VII of Ref. 25 and used the same order of molecules in our listings as in that table. An important distinction, however, is that our results are optimized for each functional, whereas the counterpart results in Ref. 25 used PBE orbitals and densities for all the functionals, i.e., those results are not self-consistent. For comparison, and to show the basis-set dependence of the results, in the Supplementary Material (see Ref. 30), the total energies and atomization energies corresponding to DZVP and TZVP orbital basis, and GEN-A2 and GEN-A2* auxiliary basis sets, using the experimental and the optimized ge-

TABLE I. Values of α and positions of the maximum in the new exchange enhancement functional, Eq. (10), for two values of the gradient parameter μ.

	μ	α	$s_{\max}$
GE	10/81	0.001 553	8.2631
PBE	0.219 516	0.002 762	6.1968

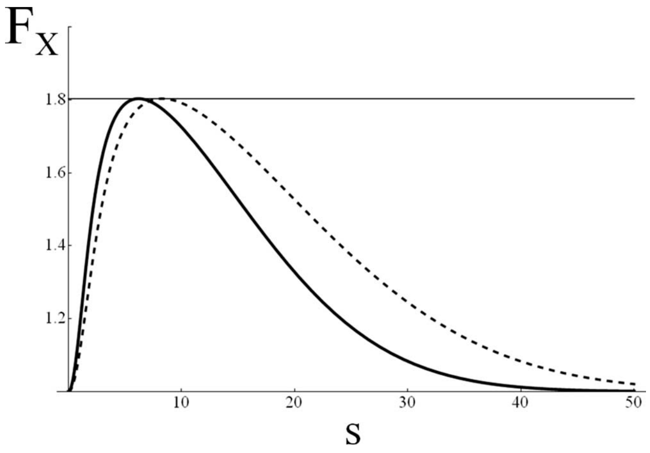

FIG. 2. Dependence of the modified exchange enhancement factor $F_{x\mathrm{VMT1}}$ upon the parameter α with respect to the LO bound (indicated by the horizontal line). The left (solid) curve corresponds to μ_{PBE}, and the right (dashed) to μ_{GE}.

ometries, as well as bond distances from the optimized structures with these orbital and auxiliary basis sets, are reported. Those data confirm that the comparisons between XC approximations discussed here are not strongly basis-set dependent (except in cases such as Be_2, a molecule which exposes the deficiencies of small basis sets quite clearly).

TABLE II. Total energies (Hartree a.u.) at the optimized geometries for the 20 molecule test set. The X functionals are the original PBE, PBEsol, and the functional proposed in this work, VMT [Eq. (10)] using μ_{PBE} and μ_{GE}. In all cases, the correlation functional used was the original PBE. VMT(μ_{PBE}) is the counterpart of PBE, and VMT(μ_{GE}) is the counterpart of PBEsol.

Molecule	PBE	VMT(μ_{PBE})	PBEsol	VMT(μ_{GE})
H_2	−1.176 016	−1.180 710	−1.157 288	−1.151 978
LiH	−8.047 069	−8.060 334	−7.973 443	−7.959 888
OH	−75.689 179	−75.719 037	−75.429 927	−75.393 292
H_2O	−76.388 093	−76.417 570	−76.127 807	−76.086 673
HF	−100.401 385	−100.432 767	−100.101 887	−100.057 223
Li_2	−14.954 428	−14.977 122	−14.826 820	−14.808 618
LiF	−107.357 079	−107.397 033	−107.000 027	−106.946 168
Be_2	−29.273 275	−29.304 306	−29.080 789	−29.056 614
CO	−113.234 655	−113.282 043	−112.824 173	−112.767 679
N_2	−109.453 337	−109.500 783	−109.046 041	−108.991 103
O_2	−150.251 205	−150.304 865	−149.760 067	−149.692 794
F_2	−199.430 765	−199.490 290	−198.846 654	−198.763 677
P_2	−682.411 115	−682.504 420	−681.248 096	−681.100 351
NO	−129.818 101	−129.868 641	−129.368 487	−129.307 288
NH_3	−56.516 009	−56.543 866	−56.290 953	−56.253 566
Cl_2	−920.036 868	−920.140 702	−918.668 665	−918.497 478
C_2H_2	−77.253 115	−77.296 232	−76.910 582	−76.859 863
C_2H_4	−78.505 863	−78.551 253	−78.149 576	−78.092 246
CH_4	−40.467 932	−40.494 265	−40.272 854	−40.238 038
HCN	−93.348 287	−93.393 545	−92.973 343	−92.920 267

TABLE III. As in Table II for the atomization energies, in kcal/mol, for the 20 molecule test set.

Molecule	Expt.[a]	PBE	VMT(μ_{PBE})	PBEsol	VMT(μ_{GE})
H_2	109.50	110.58	110.99	112.85	110.71
LiH	57.80	54.08	54.05	55.19	52.33
OH	106.40	110.58	109.27	115.04	112.59
H_2O	232.20	235.46	232.65	246.29	241.61
HF	140.80	142.60	140.9	149.58	147.04
Li_2	24.40	20.35	20.43	20.88	19.58
LiF	138.90	139.21	137.07	143.36	139.52
Be_2	3.00	9.98	9.22	11.13	10.73
CO	259.30	266.14	262.17	276.5	273.34
N_2	228.50	241.45	237.59	247.92	243.72
O_2	120.50	141.24	137.36	153.31	150.99
F_2	38.50	51.63	48.73	60.91	58.62
P_2	117.30	118.98	116.34	126.43	124
NO	152.90	169.90	166.03	178.92	175.61
NH_3	297.40	302.48	299.34	313.32	306.78
Cl_2	58.00	63.15	60.84	70.63	69.84
C_2H_2	405.40	413.14	407.8	427.83	421.89
C_2H_4	562.60	571.86	565.42	591.96	583.05
CH_4	419.30	420.97	417.5	434.42	427.29
HCN	311.90	324.19	319.58	334.76	329.53

[a] All experimental atomization energies were taken from Table VII in Ref. 25.

Three major features stand out. First, for either choice of μ, the use of the VMT form reduces the atomization MAD by 20% or a little more. This reduction is independent of the choice of the auxiliary basis set (see Fig. 3). Second, the MAD in the bond lengths differs by 0.001 Å among the functionals, perhaps because of the fact that the test set is too small to find a statistically significant difference. Similarly, for the three bond angles that were optimized with the DZ-ANO basis, the largest deviation found was 0.47° in ammonia with the VMT(μ_{GE}) X functional. The geometry MADs with the DZVP basis are more than twice those from the considerably larger DZ-ANO basis set, but the MADs in the atomization energies show the opposite trend, namely, they are smaller with the DZVP than with the DZ-ANO basis (see Table V). We suspect that this difference arises because the DZVP basis is highly optimized for the energetics of small systems treated in LDA, whereas the DZ-ANO basis, although larger, is unoptimized. The important point is that, irrespective of basis, VMT improves things. Third, shifting the value of μ from μ_{PBE} to μ_{GE} worsens the atomization energy MAD by factors of 2.2 for PBE to PBEsol and by 2.5 for VMT(μ_{PBE}) to VMT(μ_{GE}). This behavior is consistent with prior reports[3,13] and follows from the structure of the enhancement factors. In PBE and SOGGA, the value of μ is completely decoupled from the enforcement of the LO bound, whereas in VMT the value of $s_{\max}$ is a slowly decreasing function of μ for relevant values of α (recall Fig. 1). Note that, like SOGGA,[13] the VMT functional respects the second-order gradient expansion for both X and C when used with μ_{GE} and the original PBE C functional.

To characterize the variability of the results, Table V also lists the mean deviations (unsigned) and the molecules showing the least and greatest deviations from the reference data. For the atomization energies, the basis set clearly makes no difference for maximum deviation: With one exception, O_2 is always the worst. For bond lengths, there is a basis-set difference, but both maximum offenders are low mass.

TABLE IV. As in Table II for the bond lengths, in Å, for the 20 molecule test set.

Molecule	Bond	Expt.	PBE	VMT(μ_{PBE})	PBEsol	VMT(μ_{GE})
H_2		0.7414[a]	0.7501	0.7494	0.7578	0.7594
LiH		1.5949[a]	1.6009	1.6068	1.6076	1.6118
OH		0.96966[b]	0.9864	0.9869	0.9886	0.9889
H_2O	OH	0.9575[a]	0.9721	0.9722	0.9733	0.9735
HF		0.9169[a]	0.9351	0.9350	0.9357	0.9350
Li_2		2.6729[a]	2.7261	2.7252	2.7460	2.7513
LiF		1.5639[a]	1.5846	1.5887	1.5785	1.5819
Be_2		2.44[c]	2.4253	2.4366	2.4292	2.4450
CO		1.1283[a]	1.1409	1.1424	1.1393	1.1407
N_2		1.0977[a]	1.1053	1.1066	1.1041	1.1053
O_2		1.2074[a]	1.2217	1.2239	1.2147	1.2146
F_2		1.4119[a]	1.4226	1.4264	1.4065	1.4061
P_2		1.8931[a]	1.9132	1.9153	1.9080	1.9085
NO		1.1506[a]	1.1582	1.1600	1.1548	1.1557
NH_3		1.012[a]	1.0267	1.0270	1.0287	1.0293
Cl_2		1.9878[a]	2.0245	2.0277	2.0084	2.0053
C_2H_2	CH	1.06[a]	1.0699	1.0697	1.0738	1.0749
	CC	1.203[a]	1.2126	1.2137	1.2128	1.2142
C_2H_4	CH	1.087[a]	1.0914	1.0915	1.0954	1.0959
	CC	1.339[a]	1.3380	1.3397	1.3363	1.3374
CH_4	CH	1.087[a]	1.0967	1.0969	1.0997	1.1007
HCN	CH	1.0655[a]	1.0744	1.0745	1.0790	1.0800
	CN	1.1532[a]	1.1623	1.1636	1.1616	1.1630

[a] From Ref. 31.
[b] From Ref. 32.
[c] From Ref. 33.

IV. CONCLUSIONS

We have proposed and tested a nonempirical extension of the PBE GGA exchange functional that satisfies the LO bound, VMT. Instead of the normally used saturation of the PBE enhancement exchange function in the large-*s* limit, it quenches to the electron gas limit. For either choice of gradient coefficient, μ_{PBE} or μ_{GE}, the VMT enhancement factor improves atomization energies relative to PBE or PBEsol for the test set we have considered without significant impairment to the quality of the predicted equilibrium geometries. These findings suggest that there is still room to improve GGA functionals in a nonempirical way. Further testing with a larger test set and an empirical version of the functional presented here will be published elsewhere.

ACKNOWLEDGMENTS

We acknowledge valuable conversations with Klaus Capelle, Mariana Odashima, John Perdew, Adrienn Ruzsinszky, Gabor Csonka, José Luis Gázquez, Andreas Köster, and Mark Casida. A.V. was supported in part by Conacyt Grant No. 47175-F and CIAM Project No. 2005-C02-51840. V.M. was supported in part by a CONACyT Ph.D. fellow-

TABLE V. MAD, mean deviations (MD), and molecules showing the minimum and maximum deviations for the atomization energies, ΔE_{at} (kcal/mol) and the bond lengths, R (Å) for the functionals tested in this work on the 20-molecule tests set and for the DZ-ANO and DZVP orbital basis sets and the GEN-A2* auxiliary basis set.

Property	Orbital basis set		PBE	VMT(μ_{PBE})	PBEsol	VMT(μ_{GE})
ΔE_{at}	DZ-ANO	MAD	6.95	4.67	14.94	11.74
		MD	6.17	3.43	14.33	10.71
		Min, Max	Li_2, O_2	Li_2, O_2	Li_2, O_2	LiH, O_2
	DZVP	MAD	4.89	3.68	11.92	9.51
		MD	2.98	0.45	11.24	7.94
		Min, Max	Li_2, O_2	P_2, O_2	Li_2, C_2H_4	Li_2, O_2
R	DZ-ANO	MAD	0.015	0.016	0.016	0.016
		MD	0.012	0.014	0.012	0.014
		Min, Max	Be_2, Li_2	Be_2, Li_2	Be_2, Li_2	Be_2, Li_2
	DZVP	MAD	0.038	0.040	0.035	0.035
		MD	0.038	0.040	0.035	0.035
		Min, Max	C_2H_4, Be_2	C_2H_4, Be_2	F_2, Be_2	F_2, Be_2

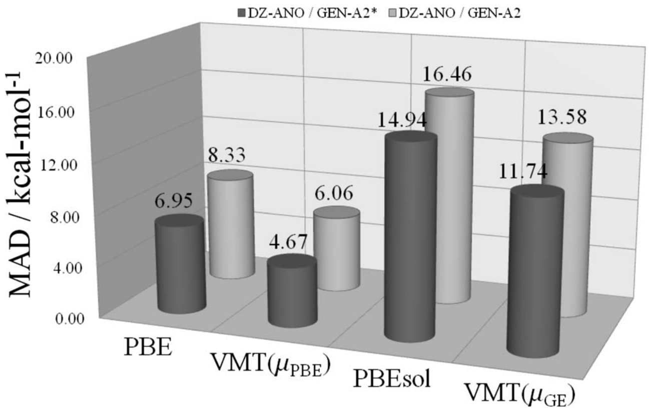

FIG. 3. Comparison of mean absolute atomization energy deviations for PBE, VMT(μ_{PBE}), PBEsol, and VMT(μ_{GE}) for the 20 molecule test set described in the text, using the DZ-ANO orbital basis set, and the GEN-A2* and GEN-A2 auxiliary basis sets.

ship. S.B.T. was supported in part by the U.S. National Science Foundation under Grant No. DMR-0325553 (ITR) and in part by CONACyT (México) Grant No. 2005-C02-51840.

[1] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996); **78**, 1396E (1997).

[2] G. I. Csonka, O. A. Vydrov, G. E. Scuseria, A. Ruzsinszky, and J. P. Perdew, J. Chem. Phys. **126**, 244107 (2007).

[3] J. P. Perdew, A. Ruzsinszky, G. I. Csonka, O. A. Vydrov, G. E. Scuseria, L. A. Constantin, X. Zhou, and K. Burke, Phys. Rev. Lett. **100**, 136406 (2008).

[4] J. P. Perdew, L. A. Constantin, E. Sagvolden, and K. Burke, Phys. Rev. Lett. **97**, 223002 (2006).

[5] P. Elliott, D. H. Lee, A. Cangi, and K. Burke, Phys. Rev. Lett. **100**, 256406 (2008).

[6] E. H. Lieb and S. Oxford, Int. J. Quantum Chem. **19**, 427 (1981).

[7] G. K.-L. Chan and N. C. Handy, Phys. Rev. A **59**, 3075 (1999).

[8] D. L. Novikov, A. J. Freeman, N. E. Christensen, A. Svane, and C. O. Rodriguez, Phys. Rev. B **56**, 7206 (1997).

[9] Y. K. Zhang and W. T. Yang, Phys. Rev. Lett. **80**, 890 (1998).

[10] B. Hammer, L. B. Hansen, and J. K. Nørskov, Phys. Rev. B **59**, 7413 (1999).

[11] E. L. Peltzer y Blancá, C. O. Rodriguez, J. Shitu, and D. L. Novikov, J. Phys.: Condens. Matter **13**, 9463 (2001).

[12] M. M. Odashima and K. Capelle, J. Chem. Phys. **127**, 054106 (2007); Int. J. Quantum Chem. **108**, 2428 (2008).

[13] Y. Zhao and D. G. Truhlar, J. Chem. Phys. **128**, 184109 (2008).

[14] L. J. Sham, in *Computational Methods in Band Theory*, edited by P. M. Marcus, J. F. Janak, and A. R. Williams (Plenum, New York, 1971), p. 458.

[15] M. Galvan and J. L. Gazquez, J. Chem. Phys. **85**, 4203 (1986).

[16] V. Medel, A. Vela, and S. B. Trickey (unpublished).

[17] A. M. Koster, P. Calaminici, M. E. Casida, V. D. Dominguez, R. Flores-Moreno, G. Geudtner, A. Goursot, T. Heine, A. Ipatov, F. Janetzko, J. M. d. Campo, S. Patchkovskii, J. U. Reveles, A. Vela, B. Zuniga, and D. R. Salahub, deMon2k, The International deMon Developers Community, Cinvestav, Mexico D. F., Mexico, 2008.

[18] P. Mlynarski and D. R. Salahub, Phys. Rev. B **43**, 1399 (1991).

[19] J. P. Perdew and W. Yue, Phys. Rev. B **33**, 8800 (1986); J. P. Perdew, *ibid.* **40**, 3399 (1989); **33**, 8822 (1986); **34**, 7406 (1986).

[20] A. Vela, *Symposium 19, XVth International Material Research Congress* (Academia Mexicana de Ciencia de Materiales, Cancun, 2006).

[21] W. P. Wang and R. G. Parr, Phys. Rev. A **16**, 891 (1977).

[22] S. B. Liu, Int. J. Quantum Chem. **106**, 1762 (2006).

[23] A. Zupan, J. P. Perdew, K. Burke, and M. Causa, Int. J. Quantum Chem. **61**, 835 (1997).

[24] M. Levy and J. P. Perdew, Phys. Rev. B **48**, 11638 (1993).

[25] J. P. Perdew, J. M. Tao, V. N. Staroverov, and G. E. Scuseria, J. Chem. Phys. **120**, 6898 (2004).

[26] R. Pouamerigo, M. Merchan, I. Nebotgil, P. O. Widmark, and B. O. Roos, Theor. Chim. Acta **92**, 149 (1995).

[27] P. Calaminici, F. Janetzko, A. M. Koster, R. Mejia-Olvera, and B. Zuniga-Gutierrez, J. Chem. Phys. **126**, 044108 (2007).

[28] A. M. Koster, J. U. Reveles, and J. M. del Campo, J. Chem. Phys. **121**, 3417 (2004).

[29] A. M. Koster, R. Flores-Moreno, and J. U. Reveles, J. Chem. Phys. **121**, 681 (2004).

[30] See EPAPS Document No. E-JCPSA6-130-032924 for total energies, atomization energies, and optimized bond lengths of the molecules in the test set. For more information on EPAPS, see http://www.aip.org/pubservs/epaps.html.

[31] *CRC Handbook of Chemistry and Physics*, 83th ed., edited by D. R. Lide (CRC, Boca Raton, FL, 2002).

[32] K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure IV. Constants of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1979).

[33] J. M. L. Martin, Chem. Phys. Lett. **303**, 399 (1999).