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Diminished gradient dependence of density functionals: Constraint satisfaction and self-interaction correction

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The Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation for the exchange-correlation energy functional has two nonempirical constructions, based on satisfaction of universal exact constraints on the hole density or on the energy. We show here that, by identifying one possible free parameter in exchange and a second in correlation, we can continue to satisfy these constraints while diminishing the gradient dependence almost to zero (i.e., almost recovering the local spin density approximation or LSDA). This points out the important role played by the Perdew-Wang 1991 nonempirical hole construction in shaping PBE and later constructions. Only the undiminished PBE is good for atoms and molecules, for reasons we present, but a somewhat diminished PBE could be useful for solids; in particular, the surface energies of solids could be improved. Even for atoms and molecules, a strongly diminished PBE works well when combined with a scaled-down self-interaction correction (although perhaps not significantly better than LSDA). This shows that the undiminished gradient dependence of PBE and related functionals works somewhat like a scaled-down self-interaction correction to LSDA. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2743985]

I. INTRODUCTION

Kohn-Sham density functional theory[1,2] is widely used in ground-state quantum chemistry and condensed matter physics because of its computational simplicity and the useful accuracy of its common semilocal approximations to the exchange-correlation energy E_{xc} as functionals of the electron spin densities $n_\uparrow(\mathbf{r})$ and $n_\downarrow(\mathbf{r})$. In terms of total electron density $n(\mathbf{r})=n_\uparrow(\mathbf{r})+n_\downarrow(\mathbf{r})$ and exchange-correlation energy density $n(\mathbf{r})\ \varepsilon_{\text{xc}}(\mathbf{r})$, this functional is

$$E_{\text{xc}} = \int d\mathbf{r}\ n(\mathbf{r})\varepsilon_{\text{xc}}(\mathbf{r}). \tag{1}$$

The simplest approximations are semilocal ones, in which $\varepsilon_{\text{xc}}(\mathbf{r})$ is constructed from the electron densities and orbitals in an infinitesimal neighborhood of $\mathbf{r}$. A ladder of semilocal approximations of increasing accuracy and complexity has been constructed nonempirically, by satisfying exact constraints on E_{xc}. The three rungs of this ladder are the local spin density approximation (LSDA),[1,3] the generalized gradient approximation (GGA) in the versions of Perdew and Wang 1991 (PW91) (Refs. 4 and 5) or Perdew, Burke, and Ernzerhof (PBE),[5,6] and the meta-GGA in the version of Tao, Perdew, Staroverov, and Scuseria (TPSS).[7]

To make semilocal functionals exact for all one-electron densities, Perdew and Zunger (PZ) proposed an orbital-by-orbital self-interaction correction (SIC).[8] Recently, we have proposed a way to scale down this SIC in many-electron regions, to improve its performance for molecules near equilibrium geometries.[9] The strength of the scaling is controlled by a non-negative parameter k, which equals 0 in the original PZ SIC. $k>0$ ensures that the correction vanishes for a uniform density, independent of the type of orbitals used. The optimal value of k may differ for different properties and functionals, but its typical suggested values lie between 1/2 and 3. Especially good results for atomic total energies, molecular atomization energies, the heights of energy barriers, bond lengths, ionization potentials, and electron affinities were obtained with LSDA-SIC(k=2), a choice with desirable formal properties (*vide infra*).[9]

The question remains whether there are any plausible modifications of PBE GGA or TPSS meta-GGA that might work even better with scaled-down SIC while keeping desirable formal properties of the functional. We show here that a diminished gradient dependence (moving PBE or TPSS in the direction of LSDA) can be achieved while satisfying most or all exact constraints; this is a result of interest in itself. We then test these diminished functionals in combination with scaled-down SIC.

II. NONEMPIRICAL SEMILOCAL FUNCTIONALS AND THE CONSTRAINTS THEY SATISFY

In LSDA, the local ingredients or arguments of $\varepsilon_{\text{xc}}(\mathbf{r})$ are just the local electron spin densities $n_\uparrow(\mathbf{r})$ and $n_\downarrow(\mathbf{r})$. $\varepsilon_{\text{xc}}(n_\uparrow,n_\downarrow)$ is taken to be the exchange-correlation energy per particle of an electron gas with uniform spin densities $n_\uparrow$ and $n_\downarrow$. This choice makes LSDA exact in the only limit in which it can be and essentially exact for densities that vary slowly over space. But LSDA also satisfies other exact conditions.[5] (a) Its exchange term scales properly under uniform scaling of the density. (b) Its exchange term also scales properly under spin scaling. (c) Its exchange and exchange-correlation energies respect the Lieb-Oxford lower bound for all possible densities. (d) Its exchange-correlation energy is almost correct for the linear response of a spin-unpolarized uniform electron gas, i.e., for small amplitude (and not too rapid) variations around the uniform density. For a discussion of the exact constraints on E_{xc} and original references for them, see Refs. 6 and 7.

The exchange-correlation energy

$$E_{\mathrm{xc}} = \frac{1}{2}\int d\mathbf{r} \int d\mathbf{r}'\ n(\mathbf{r})\frac{n_{\mathrm{xc}}(\mathbf{r},\mathbf{r}')}{|\mathbf{r}'-\mathbf{r}|} \tag{2}$$

depends upon the density $n_{\mathrm{xc}}(\mathbf{r},\mathbf{r}')$ at $\mathbf{r}'$ of the exchange-correlation hole around an electron at $\mathbf{r}$. LSDA inherits its hole density from the uniform gas, and so satisfies the hole constraints

$$n_x(\mathbf{r},\mathbf{r}') \leqslant 0, \tag{3}$$

$$\int d\mathbf{r}'\ n_x(\mathbf{r},\mathbf{r}') = -1, \tag{4}$$

$$\int d\mathbf{r}'\ n_c(\mathbf{r},\mathbf{r}') = 0, \tag{5}$$

where the sum rules (4) and (5) are for a closed system of fixed electron number. For a discussion of the exact constraints on n_{xc} and original references for them, see Refs. 4 and 5.

For an electron gas of slowly varying density, E_{xc} and n_{xc} have expansions in powers of the density gradients. The relevance of these expansions to atoms, molecules, and solids has recently been established.[10] LSDA is the zero-order term. Thus the natural second rung on Jacob's ladder of approximations is the GGA, which adds the ingredients $\nabla n_\uparrow(\mathbf{r})$ and $\nabla n_\downarrow(\mathbf{r})$ for $\varepsilon_{\mathrm{xc}}(\mathbf{r})$. The PW91 GGA starts from the gradient expansions of $n_x(\mathbf{r},\mathbf{r}')$ and $n_c(\mathbf{r},\mathbf{r}')$ to second order in ∇, and then introduces sharp radial and angular cutoffs of the spurious long-range (large $|\mathbf{r}'-\mathbf{r}|$) parts to satisfy Eqs. (3)–(5).

The PBE GGA was constructed to be similar to PW91 in the physical range of densities and gradients, but to satisfy conditions (a)–(d), plus two more: (e) The PBE correlation energy recovers the correct second-order gradient expansion for slowly varying densities. (f) Under uniform scaling to the high-density limit, the PBE GGA correlation energy properly scales to a constant for a finite system (while the LSDA diverges).

The gradient dependences of E_x^{PBE} and E_c^{PBE} are opposite in sign and partly cancel. This makes $E_{\mathrm{xc}}^{\mathrm{PBE}}$ somewhat more local than E_x^{PBE} (and also somewhat more accurate).

The third rung of the ladder is the meta-GGA, which adds the positive orbital kinetic energy densities $\tau_\uparrow(\mathbf{r})$ and $\tau_\downarrow(\mathbf{r})$ as further local ingredients of $\varepsilon_{\mathrm{xc}}(\mathbf{r})$. The TPSS meta-GGA satisfies conditions (a)–(f), plus several more: (g) The gradient expansion of E_x is correct to fourth order in ∇ for a slowly varying electron density. (h) The exchange potential is properly finite at a nucleus. (i) The exchange energy is exact for the H atom (but not for all one-electron densities). (j) The correlation energy vanishes for any one-electron density.

For the PBE GGA and the TPSS meta-GGA, smooth hole models[11,12] satisfying Eqs. (3)–(5) have been constructed.

For closed compact systems of fixed electron number, such as atoms or molecules around equilibrium, the nonempirical semilocal (sl) functionals LSDA, PBE, and TPSS provide useful and increasing accuracy for E_x, with an even better accuracy for E_{xc} due to error cancellation. But these functionals fail for open systems of fluctuating electron number, as in highly stretched A_2^+.[13–22]

III. SCALED-DOWN SELF-INTERACTION CORRECTION

The scaled-down self-interaction correction of Ref. 9 for any sl functional is

$$E_{\mathrm{xc}}^{\mathrm{SIC}} = E_{\mathrm{xc}}^{\mathrm{sl}}[n_\uparrow,n_\downarrow] - \sum_{\alpha\sigma}\chi_{\alpha\sigma}\{E_{\mathrm{xc}}^{\mathrm{sl}}[n_{\alpha\sigma},0] + U[n_{\alpha\sigma}]\}, \tag{6}$$

where

$$U[n_{\alpha\sigma}] = \frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\frac{n_{\alpha\sigma}(\mathbf{r})n_{\alpha\sigma}(\mathbf{r}')}{|\mathbf{r}'-\mathbf{r}|}. \tag{7}$$

Here $n_{\alpha\sigma}(\mathbf{r})=f_{\alpha\sigma}|\psi_{\alpha\sigma}(\mathbf{r})|^2$ is an orbital density, $f_{\alpha\sigma}$ is a Fermi occupation number, and

$$\chi_{\alpha\sigma} = \int d\mathbf{r}|\psi_{\alpha\sigma}(\mathbf{r})|^2\cdot\left(\frac{\tau_\sigma^W}{\tau_\sigma}\right)^k \leqslant 1 \tag{8}$$

is the scale-down factor. $\tau_\sigma^W=|\nabla n_\sigma(\mathbf{r})|^2/8n_\sigma(\mathbf{r})$ is the von Weizsäcker kinetic energy density for electrons of spin σ. Equation (6) reduces to the original PZ SIC of Ref. 8 when $k=0$ (making $\chi_{\alpha\sigma}=1$), and more generally for any one- or spin-paired two-electron region (where $\tau_\sigma^W/\tau_\sigma=1$, making $\chi_{\alpha\sigma}=1$). For many-electron regions, where $0\leqslant\tau_\sigma^W/\tau_\sigma<1$, any $k>0$ makes $0\leqslant\chi_{\alpha\sigma}<1$, and the PZ SIC is scaled down; as $k\to\infty$, the PZ SIC in such regions is scaled down to zero. The present choice of Eq. (8) is not unique and alternative constructions are possible.[23]

The energy-minimized SIC orbitals, unlike the Kohn-Sham orbitals, tend to localize on part of a system. Whether such localization occurs for the uniform electron gas is uncertain, although it seems likely.[24–26] If it does, the exact constraints of the semilocal functionals are expected to be preserved when k is an integer with $k\geqslant 2$ for LSDA or PBE, and $k\geqslant 3$ for TPSS. (If it does not, then only $k>0$ is needed, as also explained in Ref. 9.)

As mentioned at the end of Sec. I, the self-consistent tests of Ref. 9 showed that the formally certainly correct LSDA SIC($k=2$) is remarkably accurate for compact closed systems, while other combinations [including all PZ SIC $=$SIC($k=0$) combinations] are less successful. It was observed earlier that PZ SIC works better for LSDA than for other functionals.[27,28] Although SIC(k) gives no correction to the exact E_{xc}, it does not follow that SIC(k) results must improve with an improvement of the underlying semilocal functional (e.g., from LSDA to PBE GGA to TPSS meta-GGA). As explained in Ref. 9, these corrections involve evaluation of E_{xc} for an orbital density that contains nodes and orthogonalization tails. LSDA has a limited sensitivity to density variations. Functionals dependent explicitly on the density derivatives such as GGA and meta-GGA are more sensitive. Near the nodes of an orbital density are very large dimensionless density gradients not heavily sampled in ground-state total electron densities. This might lead to relatively poorer performance of PBE SIC(k) or TPSS SIC(k).

Since SIC(k) is exact for any one-electron density, the corrected binding energy curve for H_2^+ becomes exact. The original PZ SIC($k=0$) works well for other stretched bond situations involving open systems of fluctuating electron number, but unfortunately SIC($k=2$) typically provides only about half of the needed correction for these situations.[20,21] This has been explained[21] in terms of a generalization[8,22] of Eq. (4) to open systems of fluctuating electron number.

IV. DIMINISHED GRADIENT DEPENDENCE OF SEMILOCAL FUNCTIONALS

Here we will discuss how to diminish the gradient dependence of PBE GGA (and TPSS meta-GGA), while preserving the constraints of Sec. II. We will use atomic units ($\hbar=m=e^2=1$).

The PBE exchange energy for a spin-unpolarized density is

$$E_x^{\mathrm{PBE}}[n]=\int d\mathbf{r}\, n(\mathbf{r})\varepsilon_x^{\mathrm{unif}}(n(\mathbf{r}))F_x^{\mathrm{PBE}}(s(\mathbf{r})), \tag{9}$$

where $\varepsilon_x^{\mathrm{unif}}(n)=-3(3\pi^2 n)^{1/3}/4\pi$ is the exchange energy per electron of an unpolarized electron gas of density n, $s=|\nabla n|/2(3\pi^2)^{1/3}n^{4/3}$ is a dimensionless density gradient,

$$F_x^{\mathrm{PBE}}(s)=1+\kappa-\kappa/(1+\mu s^2/\kappa) \tag{10}$$

is an exchange-only enhancement factor, and μ is a positive constant.[6] $F_x^{\mathrm{PBE}}(s)$ varies from $1+\mu s^2$ at small s to $1+\kappa$ at large s. More generally, the PBE exchange energy is constructed from the universal spin-scaling relation

$$E_x[n_\uparrow,n_\downarrow]=(E_x[2n_\uparrow]+E_x[2n_\downarrow])/2. \tag{11}$$

Satisfaction of the Lieb-Oxford bound on E_x for all possible densities requires $\kappa\leqslant 0.804$. Close agreement (for $s\leqslant 3$) with PW91 exchange requires $\kappa=0.804$. In this paper, we propose to diminish the gradient dependence by choosing any κ in the range $0\leqslant\kappa\leqslant 0.804$. $\kappa=0$ recovers LSDA exchange.

The PBE correlation energy is

$$E_c^{\mathrm{PBE}}[n_\uparrow,n_\downarrow]=\int d\mathbf{r}\, n(\mathbf{r})[\varepsilon_c^{\mathrm{unif}}(n(\mathbf{r}),\varsigma(\mathbf{r})) + H(r_s(\mathbf{r}),\varsigma(\mathbf{r}),t(\mathbf{r}))], \tag{12}$$

where $\varepsilon_c^{\mathrm{unif}}(n,\varsigma)$ is the correlation energy per particle of an electron gas with uniform density n and relative spin polarization $\zeta=(n_\uparrow-n_\downarrow)/n$, $r_s(\mathbf{r})$ is the local Seitz radius ($n=3/4\pi r_s^3$), and t is another dimensionless electron density gradient[6] $\sim|\nabla n|/\phi n^{7/6}$, where $\phi=((1+\zeta)^{2/3}+(1-\zeta)^{2/3})/2$. Moreover,

$$H(r_s,\varsigma,t)=\gamma\phi^3\ln\left\{1+\frac{\beta}{\gamma}t^2\left[\frac{1+At^2}{1+At^2+(At^2)^2}\right]\right\}, \tag{13}$$

where β and γ are positive constants.[6] Note that $\varepsilon_c^{\mathrm{unif}}(n,\varsigma)\to\gamma\phi^3\ln(r_s)\to-\infty$ in the high-density limit. Finally,

$$A=\frac{\beta}{\gamma\alpha}[\exp(z)-1]^{-1}, \tag{14}$$

where $z=-\varepsilon_c^{\mathrm{unif}}/\gamma\phi^3$. The original PBE choice is $\alpha=1$, which closely matches PW91 correlation, and, in fact, α is invisible in Ref. 6; it is only here that $\alpha(0\leqslant\alpha\leqslant 1)$ has been introduced. The high-density limit of E_c^{GGA} for a finite system is a finite constant that diverges like $\gamma\phi^3\ln[\alpha]$ as $\alpha\to 0$. [Compare Eq. 9 of Ref. 6; see also Ref. 29]. The small-t limit ($\beta\phi^3t^2$) of H is independent of α.

The $t\to\infty$ limit is

$$\begin{aligned}H&\to\gamma\phi^3\ln\left\{1+\frac{\beta}{\gamma}A^{-1}\right\}\\&=\gamma\phi^3\ln\{1+\alpha[\exp(-\varepsilon_c^{\mathrm{unif}}/\gamma\phi^3)-1]\}.\end{aligned} \tag{15}$$

Thus α controls the large-gradient limit for correlation, as does κ for exchange. The original choice $\alpha=1$ makes $H\to-\varepsilon_c^{\mathrm{unif}}$ as $t\to\infty$, in agreement with PW91. Reducing α below 1 diminishes the gradient dependence of E_c^{PBE}, making the $t\to\infty$ limit of H fall between $-\varepsilon_c^{\mathrm{unif}}$ and 0. Moreover, $\alpha\to 0$ makes $\mathrm{H}\to 0$ so that Eq. (12) recovers LSDA correlation.

To guarantee satisfaction of the Lieb-Oxford bound on E_{xc} for all possible densities requires

$$2^{1/3}(1+\kappa)+0.7174(1-\alpha)\leqslant 2.273, \tag{16}$$

or $\alpha\geqslant 1+1.7562\ (\kappa-0.804)$.

We refer to Eqs. (10) and (14) with $0\leqslant\kappa<0.804$ and $0\leqslant\alpha<1$ as diminished PBE (dPBE). We are especially interested in dPBE SIC($k=2$), which satisfies all of the PBE constraints (a)–(f) of Sec. II [with the possible exception of constraint (c)], plus constraint (j) and a stronger version of constraint (i): Its exchange energy is exact for any one- or two-electron ground-state density.

A simpler path from GGA to LSDA is simply to scale the non-LSDA contributions to the GGA exchange and correlation energies by scale factors c_x and c_c, as in Becke's B3PW91 (Ref. 30) functional. Applied to PBE, this approach would lose the exact constraints (e) and (f) [as well as (d) when c_x differs from c_c].

The PBE parameters κ and α also appear and play the same role in the TPSS meta-GGA, which can also be diminished by reducing them. TPSS exchange contains two other parameters, c and e, that were chosen to satisfy constraints (h) and (i) from Sec. II. But with a scaled-down self-interaction correction to TPSS, these constraints will be satisfied for any positive values of c and e, which could be treated then as additional free parameters.

TABLE I. Mean absolute error (MAE) and mean error (ME) in kcal/mol for the AE6 test set of six representative atomization energies of molecules and for the BH6 test set of six representative barrier heights of chemical reactions. The mean atomization energy of AE6 is 517.2 kcal/mol, and the mean barrier height of BH6 is 11.9 kcal/mol. The functionals include the PBE hybrid (PBEh) with 25% exact exchange. The dPBE calculations use self-consistent orbitals from LSDA SIC(k=2). The 6-311+G($3df$,$2p$) basis set is used, except where smaller basis sets have been noted. Some non-dPBE values were taken from Ref. 9. 1 hartree =627.5 kcal/mol.

			AE6[a]		BH6[b]	
Functional	κ	α	ME	MAE	ME	MAE
LSDA	0.000	0.0	77.3	77.3	−17.9	17.9
dPBE GGA	0.02	0.4	74.4	74.4	−19.0	19.0
dPBE GGA	0.05	0.2	63.7	63.7	−17.2	17.2
PBE GGA	0.804	1.0	12.4	15.5	−9.5	9.5
PBE GGA[c]	0.804	1.0	11.7	14.9	−9.3	9.3
PBE GGA[d]	0.804	1.0	10.8	14.7	−9.0	9.0
PW91 GGA[d]			12.2	15.0	−9.3	9.3
TPSS meta-GGA	0.804	1.0	4.1	5.9	−8.5	8.5
TPSS meta-GGA[c]	0.804	1.0	−0.8	5.1	−8.6	8.6
TPSS meta-GGA[d]	0.804	1.0	1.9	5.8	−8.0	8.0
PBEh	0.804	1.0	0.6	6.2	−4.8	4.8
PBEh[d]	0.804	1.0	−3.3	7.2	−4.2	4.2
LSDA SIC(k=0)	0.000	0.0	57.7	60.3	−5.2	5.2
LSDA SIC(k=2)	0.000	0.0	6.7	8.6	−2.8	4.7
PBE SIC(k=0)	0.804	1.0	−13.6	17.0	−0.1	4.2
PBE SIC(k=2)	0.804	1.0	13.5	16.0	−6.5	6.5
dPBE SIC(k=2)	0.02	0.4	−8.1	12.7	−1.4	3.4
dPBE SIC(k=2)	0.05	0.2	1.6	6.0	−3.4	3.9

[a] The six molecules in the AE6 test set are SiH_4, S_2, SiO, C_3H_4 (propyne), $C_2H_2O_2$ (glyoxal), and C_4H_8 (cyclobutane).

[b] The BH6 set of barrier heights consists of the forward and reverse barriers for three reactions: $OH+CH_4 \rightarrow CH_3+H_2O$, $H+OH \rightarrow H_2+O$, and $H+H_2S \rightarrow H_2+HS$.

[c] 6-311G(d,p) basis set.

[d] 6-31G(d) basis set.

V. RESULTS FOR ATOMIZATION ENERGIES, BARRIER HEIGHTS, AND SURFACE ENERGIES

As a test of these ideas, we have chosen the AE6 test set[31] of representative atomization energies of molecules and the BH6 set[31] of representative barrier heights of chemical reactions, as also used in Ref. 9. The six molecules in the AE6 test set are SiH_4, S_2, SiO, C_3H_4 (propyne), $C_2H_2O_2$ (glyoxal), and C_4H_8 (cyclobutane). The BH6 set of barrier heights consists of the forward and reverse barriers for three reactions: $OH+CH_4 \rightarrow CH_3+H_2O$, $H+OH \rightarrow H_2+O$, and $H+H_2S \rightarrow H_2+HS$.

All calculations were carried out with the developmental version of the Gaussian molecular program.[32] Due to the heavy computational demand of SIC calculations, we have performed only non-self-consistent SIC calculations here. The dPBE calculations use self-consistent orbitals from LSDA SIC(k=2), as computed in Ref. 9. This choice was justified by showing that less than 0.2 kcal/mol differences can be observed in the mean errors (MEs) and mean absolute errors (MAEs) compared to self-consistent results. The 6-311+G($3df$,$2p$) basis sets has been used in the calculations, and the effect of the smaller basis sets 6-31G(d) and 6-311G(d,p) has been investigated.

The diminished functionals require the same CPU time and memory as their undiminished counterparts, i.e., no extra computational effort. The SIC calculations require considerable extra computational effort, as discussed in Ref. 9. The AE6 results in Table I show a moderate basis-set dependence. The strong overbinding tendency of PBE and the moderate overbinding tendency of TPSS are slightly compensated by the basis-set errors of the smaller 6-31G(d) and 6-311G(d,p) basis sets, as observed in Ref. 33. PW91 gives results very similar to and only slightly worse than those of PBE. The PBEh functional requires large basis sets for good AE6 results, as is typical for hybrid functionals.

We tested the dPBE SIC(k=2) functional for all $0 \leqslant \kappa \leqslant 0.804$ and $0 \leqslant \alpha \leqslant 1$. The best MEs and MAEs are shown in Table I. We have found that dPBE SIC(k=2) with κ =0.05 and α=0.2 gives the best atomization energies, and nearly the best barrier heights, when combined with the formally certainly correct scaled-down SIC(k=2). The best barrier heights of chemical reactions were obtained with κ =0.02 and α=0.4, although these parameters give quite poor atomization energies (see Table I). Therefore, the κ=0.05 and α=0.2 combination is optimal for the AE6 set and leads to only moderate worsening of the results for the BH6 set.

Our new dPBE SIC (k=2) results are considerably better than PBE SIC (k=2) and are slightly better than those of LSDA SIC (k=2) also shown in Table I. But the latter small improvement could be an artifact of fitting to small data sets.

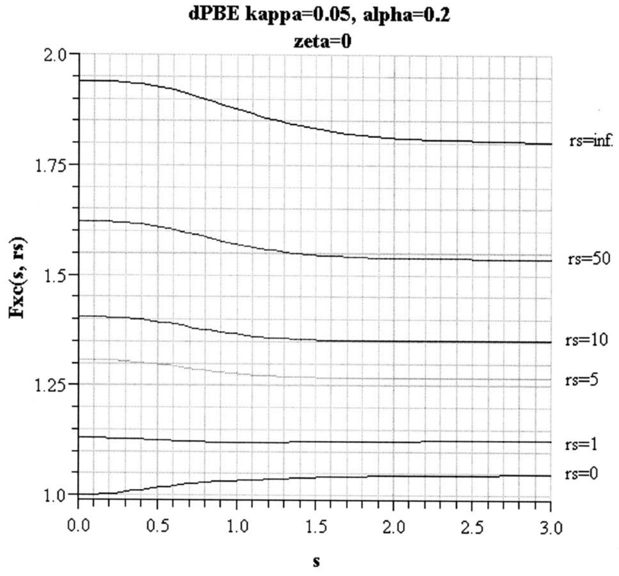

FIG. 1. Diminished PBE (dPBE) enhancement factor of Eq. (17) for fully spin-unpolarized ($\zeta=0$) densities, showing a strong resemblance to LSDA. $\kappa=0.05$ and $\alpha=0.2$, close to the optimal values for SIC($k=2$).

We also tested dTPSS SIC ($k=3$) and found that no parameter combinations gave satisfactory barrier heights. We observed in general that SIC ($k=3$) scales down the self-interaction correction too strongly; although a smaller k gives better barriers, it may be formally unsatisfactory with TPSS, as discussed in Sec. III.

For any system that is fully spin-unpolarized ($\zeta=0$) or fully polarized ($\zeta=1$), we can visualize a GGA by plotting its exchange-correlation enhancement factor F_{xc}, where

$$E_{\mathrm{xc}} = \int d\mathbf{r} n \epsilon_x^{\mathrm{unif}}(n) F_{\mathrm{xc}}(r_s, \varsigma, s). \tag{17}$$

Figures 1 and 2 plot the dPBE ($\kappa=0.05$, $\alpha=0.2$) F_{xc} versus s for various values of r_s, for the cases $\zeta=0$ and 1, respectively. The curves are nearly horizontal straight lines, very close to LSDA and not to the original PBE (Fig. 1 of Ref. 6).

Figures 3 and 4 show how the dPBE SIC($k=2$) errors depend upon κ and α for the AE6 set. The well-defined minimum is clearly visible. For the BH6 set, similar curves were produced (not shown here) with a slightly shifted minimum to $\kappa=0.02$ and $\alpha=0.4$. The BH6 MAE versus α curve is quite flat, changing only a few tenths of a kcal/mol in the range of $0.2 \leqslant \alpha \leqslant 0.5$. The results start to worsen consider-

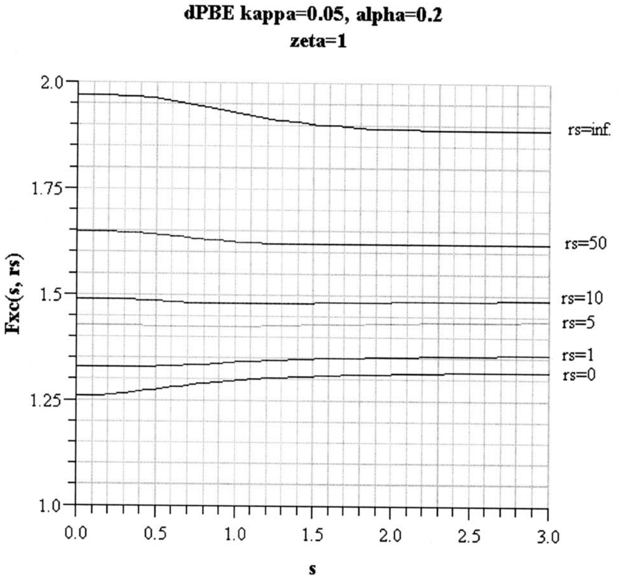

FIG. 2. Diminished PBE (dPBE) enhancement factor of Eq. (17) for fully spin-polarized ($\zeta=1$) densities, showing a strong resemblance to LSDA. $\kappa=0.05$ and $\alpha=0.2$, close to the optimal values for SIC($k=2$).

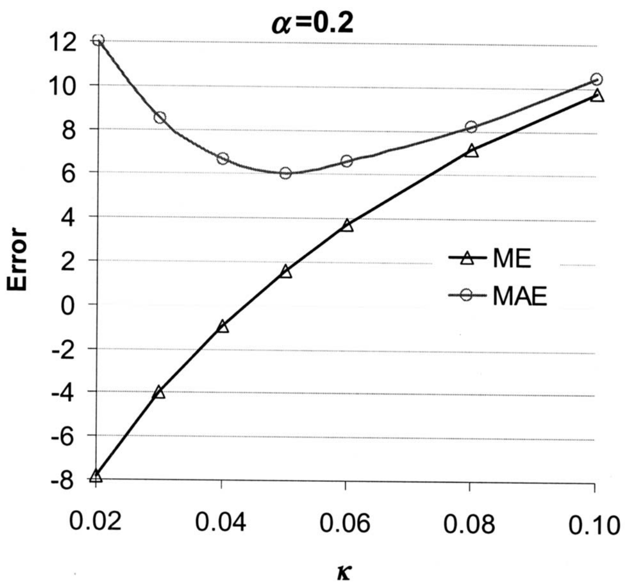

FIG. 3. Mean absolute error (MAE) and mean error (ME) of atomization energies of the AE6 test set computed with the dPBE SIC($k=2$) functionals with $\alpha=0.2$ and $0.02 \leqslant \kappa \leqslant 0.1$. All calculations use self-consistent orbitals from LSDA SIC($k=2$). The 6-311+G($3df,2p$) basis set is used. (All results are in kcal/mol.)

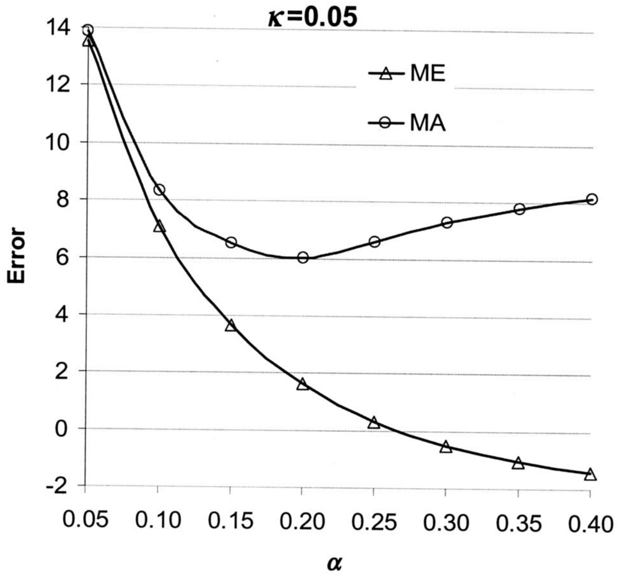

FIG. 4. Mean absolute error (MAE) and mean error (ME) of atomization energies of the AE6 test set computed with the dPBE SIC($k=2$) functionals with $0.05 \leqslant \alpha \leqslant 0.4$ and $\kappa=0.05$. All calculations use self-consistent orbitals from LSDA SIC($k=2$). The 6-311+G($3df,2p$) basis set is used. (All results are in kcal/mol.)

TABLE II. Jellium surface exchange σ_x and exchange-correlation energies σ_{xc} (erg cm^{-2}) for LSDA, dPBE($k=0.05,\alpha=0.2$), PBE, and TPSS (assumed exact, see also Ref. 12). r_s is the bulk density parameter defined in the text. Exact x values are from Ref. 40. The RPA+xc values from Ref. 41 could be as or more accurate than TPSS values ($1\ \text{a.u.}=1.557\times 10^6$ ergs cm^{-2}).

		r_s			
Method	σ	2	3	4	6
LSDA	x	3037	669	222	43.0
dPBE	x	2809	599	192	33.7
PBE	x	2438	468	128	11.8
TPSS	x	2553	498	141	15.4
Exact	x	2624	526	157	22
LSDA	xc	3354	764	261	53
dPBE	xc	3463	805	282	60.9
PBE	xc	3265	743	252	52
TPSS	xc	3380	772	266	55
RPA+	xc	3413	781	268	54

ably for $\alpha\leqslant 0.2$. The ME for the BH6 set remains always negative, showing the systematic underestimation of the barrier heights by the proposed dPBE SIC($k=2$) (see Table I). We observed that selecting the original PBE κ and decreasing α below 1 can slightly improve atomization energies over the original PBE. But this leads to a violation by dPBE of constraint (c) of Sec. II.

To see if dPBE SIC($k=2$) could also be useful for extended systems, we consider the surface exchange-correlation energy σ_{xc} of a semi-infinite jellium with a planar surface, for which the scaled-down SIC should vanish. Table II shows σ_{xc} for several bulk densities $n=3/4\pi r_s^3$. While the exact value of σ_{xc} is imperfectly known, there are reasons[34] to believe that the TPSS meta-GGA value is close to exact. Table II shows that, while PBE σ_{xc} values are too low, dPBE values are too high. However, the errors are moderate and not severe. PBE and dPBE ($\kappa=0.05$, $\alpha=0.2$) have better exchange-only σ_x contributions than does LSDA, with PBE too low and dPBE (like LSDA) too high. From Table II, it is clear that some level of diminished gradient dependence can achieve accurate exchange-correlation surface energies. In particular, the combinations dPBE ($\kappa=0.05$, $\alpha=0.1$) or dPBE ($\kappa=0.1$, $\alpha=0.2$) give surface energies that show excellent agreement with the TPSS jellium surface exchange-correlation energies σ_{xc} shown in Table II, and there are other combinations with larger $\kappa(\kappa\geqslant 0.35)$ that additionally agree with the exact σ_x.

VI. CONCLUSIONS

We have identified two parameters (κ in PBE exchange, and α in PBE correlation) that can be reduced from their original values, diminishing the gradient dependences while preserving the exact constraints satisfied by the original PBE. The best diminished PBE (dPBE) for a scaled-down self-interaction correction ($k=2$) turns out ($\kappa=0.05$, $\alpha=0.2$) to be close to LSDA. The scaled-down SIC is not available in publicly released codes, and we do not recommend it for general use without further reduction of its high cost/performance ratio.

Because the optimal dPBE is so much like LSDA, it would be easy to construct for it a LSDA-like exchange-correlation hole that satisfies Eqs. (3)–(5). Evidently then the PW91 and PBE constraints leave a lot of freedom for the gradient correction to LSDA. Nevertheless, the original PBE GGA represents a choice that depends only on fundamental constants (without empirical parameters) and also one that agrees closely with PW91, constructed using sharp real-space cutoffs of the gradient expansions for the exchange and correlation holes. When no self-interaction correction is made, the original PBE is also much more accurate for atoms and molecules than is LSDA (or dPBE).

We interpret these findings as follows: In an atom or small molecule, the density itself is cut off by the small size of the system, leading to a rapid cutoff of the long-range parts of the exchange and correlation holes. The original PW91 (based on a sharp cutoff of the long-range parts of the gradient expansions for the holes) and PBE (modeled in part upon PW91) mimic this behavior, and so build into GGA some of the same self-interaction correction to LSDA that is provided alternatively by scaled-down SIC($k=2$). In a solid the exchange-correlation hole can be more diffuse, so a dPBE intermediate between PBE and LSDA, *without* self-interaction correction, could be usefully accurate. In fact, smoothing the radial cutoff of the long-range part of the gradient expression for the hole can also diminish the gradient dependence of the GGA.[5] Starting from that observation, Refs. 35 and 36 found improved lattice constants from PBE with a diminished κ. There have been other recent constructions of GGA's exclusively for solids.[37–39]

We have found that, for the construction of useful semilocal density functionals beyond LSDA, the known universal constraints do not suffice without additional physical input (insights, fitting to data, or both). Reference 22 reaches a similar conclusion for fully nonlocal functionals that can satisfy further constraints not mentioned here. But the universal constraints still help the functionals to describe densities not envisioned by the functional developers.

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