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Local hybrids as a perturbation to global hybrid functionals

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We present new local hybrids of generalized gradient approximation exchange, designed to be small perturbations to the corresponding global hybrid. In general, local hybrids include a position-dependent admixture of nonlocal Hartree–Fock exchange. These new local hybrids incorporate a constant fraction of nonlocal exchange, plus additional nonlocal exchange contributions near nuclei. These functionals predict molecular thermochemistry and reaction barriers on average more accurately than their “parent” global hybrid. © 2009 American Institute of Physics. [doi:10.1063/1.3247288]

I. INTRODUCTION

Kohn–Sham (KS) density functional theory (DFT)^{1–4} is the most widely applied electronic structure method to chemical problems.⁵ The accuracy of predictions employing DFT strongly depends on the approximation used for the exchange–correlation (XC) functional,

$$E_{XC} = \int e_{XC}(\mathbf{r}) d^3\mathbf{r}. \quad (1)$$

Different approximations to the XC energy density $e_{XC}(\mathbf{r})$ are available. The simplest is the local density approximation (LDA), where $e_{XC}(\mathbf{r})$ is a function of the local density $\rho(\mathbf{r})$. More sophisticated generalized gradient approximations (GGAs) and meta-GGA approximations⁶ also incorporate the gradient of the density ($\nabla\rho$), its Laplacian ($\nabla^2\rho$), or the non-interacting kinetic energy density (τ),

$$\tau(\mathbf{r}) = \frac{1}{2} \sum_i |\nabla\phi_i(\mathbf{r})|^2. \quad (2)$$

Here $\phi_i(\mathbf{r})$ are the KS orbitals. Throughout this paper we will suppress spin indices for conciseness and assume quantities like ρ , ϕ , $\nabla\rho$, $\nabla^2\rho$, and τ to be either spin-up or spin-down.

The development of global hybrid functionals paved the way of DFT into the chemical community. Global hybrid functionals⁷ incorporate a constant fraction of nonlocal Hartree–Fock-type (HF) exchange,

$$E_{XC}^{\text{Gh}} = \zeta E_X^{\text{HF}} + (1 - \zeta) E_X^{\text{DFA}} + E_C^{\text{DFA}}. \quad (3)$$

Here E_X^{HF} is the HF exchange energy and E_X^{DFA} and E_C^{DFA} are the exchange and correlation energies calculated by a semilocal density functional approximation (DFA). Admixing of a fraction of HF exchange into the XC functional simulates some nondynamical correlation effects,^{8–15} and is formally justified by adiabatic connection arguments.^{7,16} No constant fraction of HF exchange was found to describe all properties well.¹⁷ More HF exchange is desirable for barrier heights and less HF exchange is favorable for thermochemistry.^{18,19} Additionally, the optimum amount of HF exchange varies with

the DFA. LDA usually (but not always²⁰) needs more HF exchange than GGAs, which need more than meta-GGAs.

A possible solution to this problem is the incorporation of a position dependent fraction $f(\mathbf{r})$ of HF exchange,^{21,22}

$$E_{XC}^{\text{Lh}} = \int [f(\mathbf{r}) e_X^{\text{HF}}(\mathbf{r}) + [1 - f(\mathbf{r})] e_X^{\text{DFA}}(\mathbf{r})] d^3\mathbf{r} + E_C^{\text{DFA}}. \quad (4)$$

Here $e_X^{\text{DFA}}(\mathbf{r})$ is the exchange energy density calculated by a semilocal DFA. The HF exchange energy density $e_X^{\text{HF}}(\mathbf{r})$ in the conventional gauge^{22,23}

$$e_X^{\text{HF}}(\mathbf{r}) = -\frac{1}{2} \sum_{i,j} \phi_i^*(\mathbf{r}) \phi_j(\mathbf{r}) \int \frac{\phi_j^*(\mathbf{r}') \phi_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}' \quad (5)$$

is constructed from the occupied KS or generalized Kohn–Sham (GKS) orbitals. The first implementation of this “local hybrid” ansatz was reported by Jaramillo *et al.*²¹ in 2003, who proposed and implemented a local hybrid with the mixing function

$$f(\mathbf{r}) = \frac{\tau_{\text{w}}(\mathbf{r})}{\tau(\mathbf{r})}, \quad (6)$$

$$\tau_{\text{w}}(\mathbf{r}) \equiv \frac{|\nabla\rho(\mathbf{r})|^2}{8\rho(\mathbf{r})}. \quad (7)$$

This mixing function incorporates 100% HF exchange in one-electron regions, where HF exchange is the exact XC functional. It admixes no HF exchange in regions of constant density, including the uniform electron gas where semilocal exchange is exact. This local hybrid showed very promising barrier heights and dissociation behaviors of two-center three-electron bonds, but unfortunately rather poor thermochemistry results. Later, Kaupp *et al.*^{19,24,25} reported that parametrized mixing functions including

$$f(\mathbf{r}) = \alpha_1 \frac{\tau_{\text{w}}(\mathbf{r})}{\tau(\mathbf{r})}, \quad (8)$$

$$f(\mathbf{r}) = \left(\frac{s}{\alpha_2 + s} \right)^2, \quad (9)$$

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$$s(\mathbf{r}) = \frac{|\nabla\rho(\mathbf{r})|}{2(3\pi^2)^{1/2}\rho^{4/3}(\mathbf{r})}, \quad (10)$$

or

$$f(\mathbf{r}) = \text{erf}(\alpha_3 s), \quad (11)$$

(where α_1 , α_2 , and α_3 are empirical parameters) combined with LDA exchange can provide accurate thermochemistry and reaction barriers. The use of a density matrix similarity metric showed promise for constructing local hybrids of LDA and GGA exchange.^{26,27} Recently, Perdew and co-workers²⁸ proposed the competitive local hybrid (“hyper-GGA”) PSTS (Perdew–Staroverov–Tao–Scuseria) for thermochemistry and barrier heights by hybridizing the meta-GGA TPSS (Tao–Perdew–Staroverov–Scuseria) with HF exchange using five empirical parameters.²⁹ PSTS is an improvement over TPSS for thermochemistry and kinetics. Compared to its “parent” global hybrid TPSSh (90% TPSS and 10% HF exchange), PSTS is slightly inferior for thermochemistry but significantly better for reaction barriers.³⁰

Local hybrid functionals were implemented self-consistently within the LHF/CEDA (localized Hartree-Fock/common energy denominator) approximation to OEP (optimized effective potential) by Arbuznikov *et al.* in 2006.³¹ This self-consistent localized local hybrid (LLH) method was later extended and applied in calculations of nuclear shielding constants.³² The implementation is computationally demanding, requiring two separate resolutions of the identity to construct the averaged local potential entering the LLH equations. Most subsequent thermochemical tests of local hybrids have been performed non-self-consistently.^{19,24–27,33} Recently, self-consistent local hybrids were implemented within the GKS scheme,³⁴ which requires just one resolution of the identity and is computationally more tractable.

Range-separated functionals^{35–59} are another possibility to overcome the limitations of global hybrids. They separate the Coulomb operator into at least two parts and treat each part differently. In this work, we will only consider the partition of the Coulomb operator in two different parts, a short-range (SR) and a long-range (LR) component,

$$\frac{1}{|\mathbf{r}-\mathbf{r}'|} = \underbrace{\frac{\text{erfc}(\omega|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|}}_{\text{SR}} + \underbrace{\frac{\text{erf}(\omega|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|}}_{\text{LR}}. \quad (12)$$

Here erf is the standard error function and erfc its complement, which are chosen for computational convenience. The very accurate long-range-corrected LC- ω PBE uses 100% HF exchange in the LR and 100% PBE (Perdew–Burke–Ernzerhof) exchange in the SR,³⁹

$$E_{\text{XC}}^{\text{LC-}\omega\text{PBE}} = E_{\text{X}}^{\text{SR-PBE}} + E_{\text{X}}^{\text{LR-HF}} + E_{\text{C}}^{\text{PBE}}. \quad (13)$$

The other limiting case is represented by the screened (SC) HSE functional, which incorporates 100% PBE exchange in the LR and 25% HF exchange in the SR.⁴⁴ The HISS (Henderson–Izmaylov–Scuseria–Savin) functional⁵³ partitions the Coulomb operator in three parts by adding a middle-range (MR), and uses 100% PBE exchange in the SR

and LR with 60% HF exchange and 40% PBE exchange in the MR.

Recently, SC as well as LC LDA functionals were locally hybridized in the SR.³⁴ Functionals with a universal range-separation parameter ω have obvious limitations. Krukau *et al.*⁵⁷ extended the concept to locally range-separated (LRS) functionals with a position-dependent $\omega(\mathbf{r})$. The proposed LRS- ω LDA functional outperforms its “parent” LC- ω LDA for thermochemistry and kinetics.

In this work, we report local hybrid functionals that act as a perturbation to global hybrid functionals. Our goal is to create local hybrids of GGA exchange that are at least as accurate as the corresponding global hybrid functionals. The main focus of the present study is the concept of a local hybrid as a perturbation to a global hybrid. We will point out its merits and failures for thermochemistry and kinetics of main group compounds. In Sec. II we describe the proposed local hybrid functionals. Section III presents details about our calculations. In Sec. IV the performance of the proposed local hybrids is compared to existing local hybrids and popular global hybrids as well as pure DFAs and an analysis of the proposed local hybrids will be presented. Finally, we will give our conclusions in Sec. V.

II. THEORY

The basic idea of our present work is twofold. First, most properties of chemical relevance are improved by a constant admixture of HF exchange. Thus, local hybrids may benefit from including some nonzero amount of HF exchange at each point in space. Second, existing semilocal approximations for exchange are generally constructed as expansions about slowly varying densities. Such approximations should tend to work less well in regions with strongly varying densities, such as near the nuclei. Semilocal approximations and popular global hybrids were shown^{43,47,49,60,61} to fail where the potential of density tail regions is important because they exhibit the wrong decay of the XC potential.^{62,63} Additionally, examination of existing successful local hybrid mixing functions^{19,24–27} shows that they typically include relatively large admixtures of HF exchange near nuclei and in stretched bonds.

Based on these ideas, we propose a new local hybrid mixing function that combines a constant fraction of HF exchange with Gaussian-type functions centered at all atoms. The fraction of HF exchange is heuristically given by Eq. (14),

$$f(\mathbf{r}) = \zeta + (1 - \zeta) \text{erf}\left(C \sum_A e^{-\gamma|\mathbf{r}_A|^2}\right), \quad (14)$$

$$\zeta_{\text{PBE}} = \frac{1}{4}.$$

The positive parameter ζ determines the base fraction of HF exchange, $|\mathbf{r}_A|$ is the distance of the reference point to nucleus A , and the positive coefficient C switches the contribution of the nuclei on and off. Additionally, it can be used to include system-specific information. The sum loops over all nuclei A in the molecule. The erf function provides a suitable mapping of the sum of all atomic contributions between

TABLE I. Definition of the parameters of the local hybrid mixing functions proposed in this work. All three local hybrids use $\zeta = \zeta_{\text{PBE}} = \frac{1}{4}$ in Eq. (14).

Functional	Parameters	
	C	γ
Lh1-PBE	1	16
Lh2-PBE	erf(s)	17
Lh3-PBE	erf(s)	30τ

0 and 1 which becomes important for molecules.

The positive parameter γ can contain other system-specific ingredients. It was fitted within the AE6 (six atomization energies) and BH6 (three forward and reverse hydrogen transfer barrier heights) test sets⁶⁴ to minimize the average mean absolute error (AMAE),

$$\text{AMAE} = \frac{\text{MAE}(\text{AE6}) + \text{MAE}(\text{BH6})}{2}. \quad (15)$$

The AMAE is only intended to be used within the optimization process for the adjustable parameter and not as a quality criterion for the given density functional. Table I shows the definitions of the parameters of the proposed local hybrid mixing functions. The proposed local hybrids add one empirical parameter to the underlying global hybrid PBEh^{65,66} (identical to PBE0 and PBE1PBE), which is usually considered to be a nonempirical DFA.⁶⁷

Due to the incorporation of the noninteracting kinetic energy density τ in Lh3-PBE, the contributions around the atoms become very narrow. With Lh1-PBE containing no system-specific information, Lh2-PBE including the dimensionless density gradient s ,^{68,69} and Lh3-PBE comprising s and the local kinetic energy density τ , we present local hybrids with a LDA-like mixing function (Lh1-PBE), with a GGA-like mixing function (Lh2-PBE), and with a meta-GGA-like mixing function (Lh3-PBE).

Figure 1 shows the dependence of the mean absolute errors (MAE) within the AE6 and BH6 test sets on the parameter γ . The MAE values are quite insensitive to the precise value of the parameter γ , especially for Lh3-PBE. The atomization energies depend more on its value than the barrier heights. In fact, the minimum of the AMAE is dominated by the dependence of the MAEs of the AE6 test set on γ .

Figure 2 shows the local mixing function for propyne along the linear C-C-C-H axis for Lh1-PBE (dashed line) and Lh3-PBE (solid line) in self-consistent calculations. Results are compared to the t -LMF local mixing function (LMF) of Refs. 19,24 [Eq. (16), below], which provides accurate local hybrids of LDA exchange. The implementation of our self-consistent algorithm for local hybrids was presented previously.³⁴ Figure 3 displays the local mixing function for N_2 at four different atomic distances for Lh3-PBE (solid line) and t -LMF (dotted line). The amount of HF exchange around the bond midpoint admixed into the XC functional of both local hybrids increases with the atomic distance [cf. Figs. 3(b)–3(d)]. Lh3-PBE exhibits very narrow, spiky contributions at the nuclei due to the high values of τ near the nuclei for atoms heavier than He. Numerical tests show that they give negligible contributions to energies and properties.

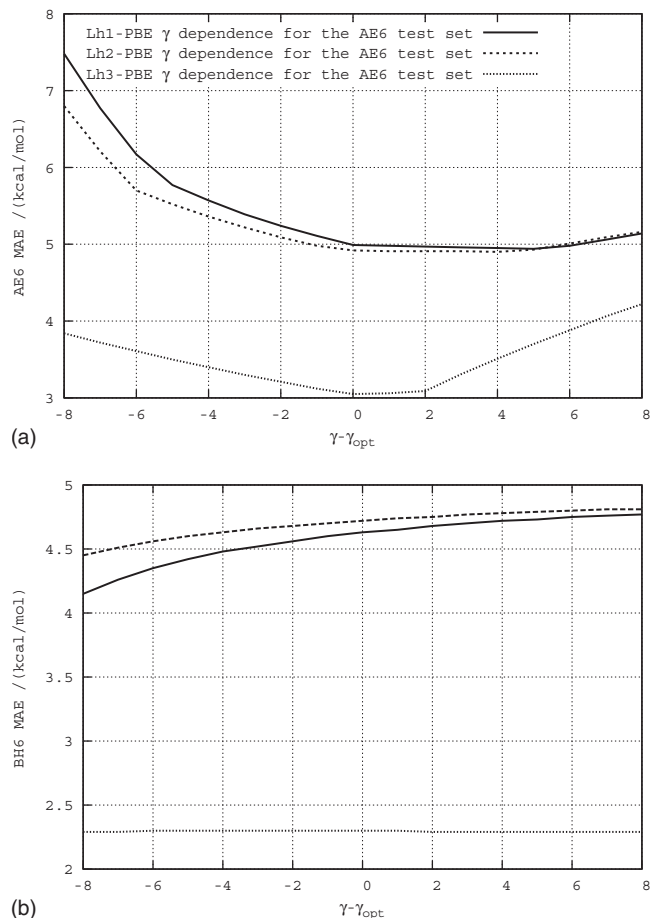


FIG. 1. Dependence of the MAE values within the AE6 and BH6 test sets on the parameter γ .

Lh1-PBE obeys the same exact constraints as PBEh. The situation is more difficult for Lh2-PBE and Lh3-PBE. They do not obey the low-gradient condition,⁷⁰ which requires the mixing function to pass into the homogeneous limit with a vanishing slope. This is related to the requirement of the gradient expansion of the exchange energy density to comprise only even powers of the dimensionless density gradient.²⁵ Both, Lh2-PBE and Lh3-PBE will go with a leading linear term (i.e., with an odd power of the dimensionless

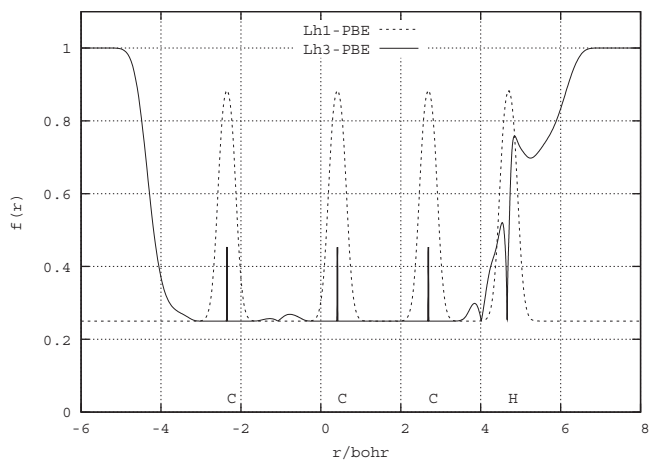


FIG. 2. Local mixing function for propyne along the linear C-C-C-H axis for Lh1-PBE (dashed line) and Lh3-PBE (solid line).

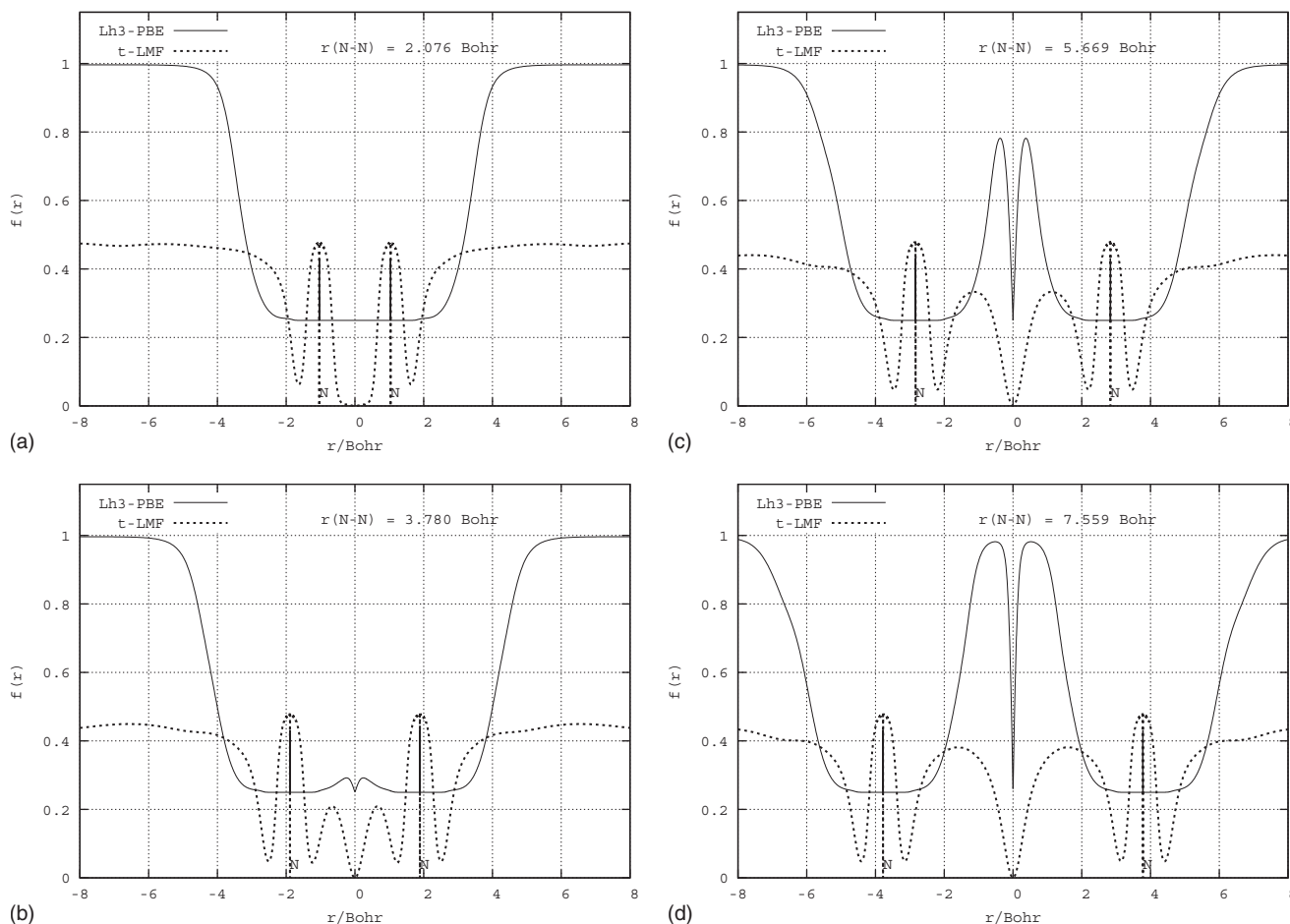


FIG. 3. Local mixing functions for N_2 of Lh3-PBE (solid line) and t -LMF (dotted line) for different distances.

density gradient) in its Taylor expansion to the homogeneous limit. Therefore, they will not have a vanishing slope at the transition to the homogeneous limit. We explored $\text{erf}(s^2)$ instead of $\text{erf}(s)$ as a scaling function for Lh3-PBE. That ansatz would obey the low-gradient condition as it would have a leading quadratic term in its Taylor expansion, but the results were deteriorated.

Neither t -LMF nor Lh1-PBE nor Lh2-PBE obey the asymptotic limit of $f(\mathbf{r}) \rightarrow 1$ at points \mathbf{r} far from a finite system. The mixing function of PSTS (Ref. 29) and those obtained from density-matrix similarity metrics^{26,27} do. Far from a finite system, τ decays faster to zero than $|\mathbf{r}_A|^2$ goes to infinity, and $\text{erf}(s)$ goes to 1. Thus, the asymptotic limit of Lh3-PBE is given by

$$\lim_{|\mathbf{r}| \rightarrow \infty} f(\mathbf{r}) = \zeta + (1 - \zeta)\text{erf}(N_{\text{atoms}}).$$

Here, N_{atoms} is the number of atoms in the molecule. Thus for $\zeta=0.25$ asymptotically, 88.2% HF exchange are mixed with 11.8% semilocal exchange for atoms, 99.7% HF exchange with 0.3% semilocal exchange for diatomics, and effectively 100% HF exchange for triatomics and larger molecules. Therefore, Lh3-PBE obeys the constraint of the asymptotic decay for the exchange potential in the case of triatomics or larger molecules. We tried to employ other mapping functions which reach the asymptotic limit of 99.7% HF exchange with 0.3% semilocal exchange already for atoms, but

the local hybrids based on those mapping functions were degraded in the overall performance.

The dependence on the number of atoms in the system causes the formal loss of size consistency of the method for Lh3-PBE. Test calculations on He, Ne, Ar, and selected systems from the AE6 and BH6 test sets showed that errors introduced by the nonsize consistency are well below 0.1 kcal/mol. As the dependence on the number of atoms becomes important mainly for density tail regions, we expect that this is not severe.

III. COMPUTATIONAL DETAILS

We have implemented the expression (14) in the different variants as shown in Table I into the development version of the GAUSSIAN electronic structure program.⁷¹ All calculations employ the fully uncontracted 6-311++G(3df,3pd) basis set^{72,73} to obtain benchmark quality results. Test calculations showed that the results vary only slightly using the much larger uncontracted aug-cc-pVQZ basis set.⁷⁴ For numerical integration of the DFT XC potential, we use the UltraFine grid with 99 radial shells and 590 angular points, except those for the plots of the local mixing functions, where a grid of 999 radial shells and 590 angular points was used. Test calculations showed that a grid with more than 99 radial shells gives the same relative energies up to the preci-

TABLE II. MEs and MAEs for the AE6 and BH6 test sets in kcal/mol.

Functional	AE6		BH6	
	ME	MAE	ME	MAE
PBE	11.8	15.1	-9.6	9.6
PBEh	0.3	6.2	-4.9	4.9
Lh1-PBE	-3.1	5.0	-4.6	4.6
Lh2-PBE	-2.8	4.9	-4.7	4.7
Lh3-PBE	-2.4	3.1	-2.3	2.3

sion reported here. All presented calculations were carried out self-consistently as described in Ref. 34.

We tested three local hybrid functionals defined by Eq. (14) and Table I in combination with PBE.⁷⁵ Some test calculations also hybridized the LDA^{76,77} [Vosko–Wilk–Nusair correlation functional number V (Ref. 77) was used] and the TPSS (Ref. 28) meta-GGA functionals. The local hybrid functionals which hybridize PBE were tested for enthalpies of formation ($\Delta_f H_{298}^\circ$) within the G2/97 (148 molecules),⁷⁸ G3-3 (75 molecules),⁷⁹ and the combination of both G3/99 (223 molecules)⁸⁰ test sets. B3LYP/6-31G(2df,p) geometries and zero-point energies with a frequency scale factor of 0.9854 were used, as recommended in Ref. 81. Additionally, we assessed the performance for reaction barrier heights using the HTBH38/04 and NHTBH38/04 test sets^{82,83} (19 forward and reverse hydrogen and nonhydrogen transfer barrier heights, respectively). The molecular geometries of the AE6, BH6, HTBH38/04, and NHTBH38/04 test sets are evaluated at the QCISD/MG3 level of theory.⁸⁴⁻⁸⁷

The proposed local hybrid functionals are compared to B3LYP,^{9,88,89} PBE,⁷⁵ PBEh,^{65,66} TPSSh,⁹⁰ LC- ω PBE,³⁹ and to two other local hybrid functionals,

$$f(\mathbf{r}) = 0.48 \frac{\tau_W}{\tau}, \quad (16)$$

hybridizing LDA^{76,77} (t -LMF^{19,24}) and

$$f(\mathbf{r}) = \left(\frac{s}{0.73 + s} \right)^2 \quad (17)$$

hybridizing SLYP^{76,89} (s -LMF^{19,25}).

Calculations of open-shell species were carried out spin unrestricted. All used geometries, zero-point energies, and reference values are available as supplementary information.⁹¹ Errors are reported as *calculated-reference*.

IV. RESULTS

Table II shows the MEs and MAEs of the proposed local hybrids, PBE, and PBEh within the AE6 and BH6 test sets, which were used to fit the parameter γ . Lh3-PBE performs best among those functionals. Interestingly, Lh1-PBE and Lh2-PBE perform quite similarly. We tried to treat ζ as an adjustable parameter for Lh1-PBE, which only deteriorated the overall performance. By choosing a higher value than 0.25 we improved barrier heights, but worsened atomization energies. Changing ζ to a lower value than 0.25 led to higher MAEs for the AE6 and BH6 test sets. We also expect to lower the likelihood of overfitting with one instead of two adjustable parameters considering the small training set with twelve reference values.

We also considered local hybrids of LDA and TPSS exchange. Both, Lh1-LDA ($\zeta^{\text{LDA}}=0.6$) and Lh1-TPSS ($\zeta^{\text{TPSS}}=0.1$) are no improvement over the corresponding global hybrids with constant HF exchange admixtures of 60% for LDA and 10% for TPSS, respectively. For Lh1-LDA, we obtained lower mean absolute errors in barrier heights than with Lh1-PBE but significantly higher mean absolute errors in atomization energies, also when treating ζ as an adjustable parameter. Lh1-TPSS yields higher MAEs for the AE6 and BH6 test sets than Lh1-PBE. Therefore, we reject other DFAs than PBE for this local hybrid ansatz.

Table III shows the ME and MAE values for the proposed local hybrids for predicting the enthalpies of formation ($\Delta_f H_{298}^\circ$, Ref. 94) for the G2/97, G3-3, and G3/99 test sets and compares them to the ME and MAE values of B3LYP, PBE, PBEh, TPSSh, LC- ω PBE, t -LMF, and s -LMF. All pro-

TABLE III. MEs and MAEs for standard enthalpies of formation ($\Delta_f H_{298}^\circ$) of the G2/97, G3-3, and G3/99 test sets in kcal/mol.

Functional	G2/97		G3-3		G3/99	
	ME	MAE	ME	MAE	ME	MAE
PBE	-16.1	16.9	-32.6	32.6	-21.6	22.2
PBEh	-2.6	5.0	-9.6	10.4	-4.9	6.8
Lh1-PBE	1.1	4.0	-2.2	6.0	0.0	4.6
Lh2-PBE	0.8	3.9	-2.7	6.1	-0.4	4.6
Lh3-PBE	0.5	3.0	1.2	3.7	0.8	3.2
t -LMF ^{a,b}	-2.5	4.2	-1.2	3.3	-2.1	3.9
s -LMF ^b	-3.9	5.1	-9.6	9.7	-5.8	6.7
LC- ω PBE ^a	-0.4	3.9	-2.0	5.2	-0.9	4.3
B3LYP	0.9	3.1	7.9	8.2	3.3	4.8
TPSSh	-1.9	4.4	-1.0	3.5	-1.6	4.1

^aReference 92.

^bReference 93.

TABLE IV. MEs and MAEs for reaction barrier heights of the HTBH38/04 and NHTBH38/04 test sets in kcal/mol.

Functional	HTBH38/04		NHTBH38/04	
	ME	MAE	ME	MAE
PBE	-9.7	9.7	-8.5	8.6
PBEh	-4.7	4.7	-3.2	3.7
Lh1-PBE	-4.4	4.4	-2.9	3.4
Lh2-PBE	-4.5	4.5	-3.0	3.5
Lh3-PBE	-1.9	2.4	-1.9	2.5
<i>t</i> -LMF ^a	-2.5	2.8	-1.9	2.5
<i>s</i> -LMF ^a	-6.0	6.0	-4.0	4.4
LC- ω PBE ^a	-0.5	1.3	1.4	2.4
TPSSh	-6.4	6.4	-6.9	7.0
B3LYP	-4.5	4.6	-4.6	4.7

^aReference 93.

posed local hybrids outperform the parent PBEh in the G3/99 test set and its subsets G2/97 and G3-3. According to the MAEs in the G3/99 test set, Lh3-PBE performs best, although it shows a slight deterioration in the G3-3 subset. All tested pure DFAs and global hybrids show a strong degradation in the G3-3 test set except TPSSh. As a matter of fact, TPSSh has a lower MAE in the G3-3 test set than in the G2/97 and G3/99 test sets, like *t*-LMF. This remarkable property of TPSSh was reported previously by Staroverov *et al.*⁹⁰ It is interesting to note that the spread of the MAE within the G3/99 test set and its subsets G2/97 and G3-3 is 0.9 kcal/mol for TPSSh and *t*-LMF. Lh3-PBE has a slightly lower MAE spread with 0.7 kcal/mol. The absolute values of the MEs for the G3/99 test set of the proposed local hybrids are all below 1 kcal/mol, which suggests an almost statistical distribution of errors rather than a systematic error of under- or overbinding. Some systematic problems of the approach are disclosed by analyzing particular errors of the functionals, e.g., SF₆ and PF₅ have a negative error for PBE of -33.2 and -11.2 kcal/mol, respectively. PBEh overcorrects the error and yields a slightly positive error of 3.1 kcal/mol for SF₆ and a significantly positive error of 12.9 kcal/mol for PF₅. Any hybrid density functional admixing even more HF exchange for these compounds than PBEh will typically have even larger errors in these cases. On the other hand side, molecules like chlorobenzene, naphthalene, pyrimidine, and tetrafluoroethylene have significant negative errors for PBE and PBEh. The latter cases are the majority which explains why the proposed concept yields an overall improvement for atomization energies on average, but it does not provide a consistent improvement for all molecules. This also shows the need for more sophisticated local hybrids.

Table IV reports the ME and MAE values for barrier heights of the HTBH38/04 and NHTBH38/04 test sets. As seen for thermochemistry, the proposed local hybrids also perform somewhat better than the parent PBEh for reaction barrier heights. The best performance in both barrier height test sets is obtained with LC- ω PBE. All local hybrids outperform any global hybrid in Table IV except *s*-LMF, which is slightly worse than PBEh for the nonhydrogen transfer bar-

riers and inferior compared to PBEh and B3LYP for the hydrogen transfer barriers. The best local hybrid for both barrier height test sets is Lh3-PBE, closely followed by *t*-LMF. For the HTBH38/04 test set, PBE and PBEh show only negative errors. We found only one slight overcorrection where Lh3-PBE shows a higher absolute error of the barrier height than PBEh. This case is the reaction NH₂+C₂H₅→C₂H₆+NH. Concerning the NHTBH38/04 test set, we found less severe and fewer cases where Lh3-PBE yields higher absolute errors than PBEh compared to the G3/99 test set, but more compared to the HTBH38/04 test set. It is interesting to note that all barriers of the reactions comprising Cl⁻ and some containing F⁻ are slightly worse described by Lh3-PBE than by PBEh, which is consistent with our observation of the severe overcorrections of the atomization energies for SF₆ and PF₅ of the G3/99 test set. Especially, the barrier of the reaction N₂+OH→H+N₂O and the barrier of the degenerate reaction H+HF→HF+H benefit from the description by Lh3-PBE compared to PBEh.

We would like to emphasize that the most important part of the presented local hybrids is not the improved performance over popular global hybrids. The more interesting part is the underlying concept of a local hybrid as a perturbation to a global hybrid and thereby improving its overall performance on average. In the following, we would like to analyze the functionals in more detail.

Lh1-PBE is the simplest form of the proposed ansatz, and it already improves over PBEh. The improvement of Lh1-PBE over PBEh validates our concept of admixing more HF exchange near the nucleus. Unexpectedly, using a system-specific scaling function (erf(*s*)) does not improve the overall performance. Lh3-PBE on the other hand side, performs better than Lh2-PBE and Lh1-PBE although admixing no significant contribution of HF exchange near to the nuclei heavier than He except the base amount ζ . Instead, it admixes additional amounts of HF exchange in stretched bond situations, for radicals, and in the asymptotic region. Our test calculations omitting the spiky contributions at the nuclei for Lh3-PBE support the assumption that the amount of HF exchange admixed within the inner core region cancels out for the calculation of relative energies in the cases of heavier atoms than He. It is also supported by chemical intuition because the main changes of the electron density will most likely occur in the valence region upon formation of a chemical bond and not in the core region.

Dividing the valence region into a core-valence and a bond-valence region opens the possibility of an additional interpretation of our results. It is obviously possible to improve over PBEh by admixing additional amounts of HF exchange in the core-valence region or in the asymptotic and in the bond-valence region in unusual situations (stretched bonds, radical character). The latter provides at least for the discussed local hybrids a better overall performance than just admixing additional HF exchange in the core-valence region.

V. CONCLUSIONS

We have introduced three new local hybrid functionals based on the ansatz of a perturbation to the accurate PBEh

global hybrid. Being a perturbation to a global hybrid constitutes our main interest in these local hybrids. Simply adding a nonsystem-specific fraction of HF exchange around the nuclei (Lh1-PBE) improves upon PBEh for thermochemistry and reaction barriers, at the cost of one additional empirical parameter. The best performance overall among these three functionals is delivered by Lh3-PBE, which scales the local mixing function with the standard error function of the dimensionless density gradient $\text{erf}(s)$ and includes the noninteracting kinetic energy density τ in the exponent. The combination of both ingredients is crucial for the improvement over Lh1-PBE and Lh2-PBE, which perform quite similarly. In contrast to previous local hybrids, the tested functionals perform better when hybridizing PBE instead of LDA. As a matter of fact, these functionals are the first local hybrids, which perform better for thermochemistry and reaction barrier heights than popular global hybrids when hybridizing a GGA. The analysis of our results showed that the presented local hybrids improve on average over their parent global hybrid PBEh, but they do not provide a consistent improvement for all tested systems. Some problematic cases were pointed out. This can be generalized to similar variants, which admix additional amounts of HF exchange on top of PBEh. Although the improvement over existing local hybrids is minor, we consider the presented results encouraging and plan to combine these and similar mixing functions with range-separation in future work.

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