

# Development of density functionals for thermochemical kinetics

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A density functional theory exchange-correlation functional for the exploration of reaction mechanisms is proposed. This functional, denoted BMK (Boese-Martin for Kinetics), has an accuracy in the 2 kcal/mol range for transition state barriers but, unlike previous attempts at such a functional, this improved accuracy does *not* come at the expense of equilibrium properties. This makes it a general-purpose functional whose domain of applicability has been extended to transition states, rather than a specialized functional for kinetics. The improvement in BMK rests on the inclusion of the kinetic energy density together with a large value of the exact exchange mixing coefficient. For this functional, the kinetic energy density appears to correct “back” the excess exact exchange mixing for ground-state properties, possibly simulating variable exchange. © 2004 American Institute of Physics. [DOI: 10.1063/1.1774975]

## I. INTRODUCTION

In the last decade, density functional theory (DFT) has probably become the number one applied computational chemistry tool. Most exchange-correlation functionals currently used<sup>1–6</sup>—including the exceedingly popular Becke 3-parameter-Lee-Yang-Parr (B3LYP) hybrid functional<sup>6,7</sup>—have been developed more than ten years ago. Yet these first-generation functionals exhibit a number of chemically important weaknesses.

A number of second-generation functionals have been proposed as successors in recent years, such as PBE (Perdew-Burke-Ernzerhof<sup>8</sup>), mPW91 [modified Perdew-Wang 1991 (Ref. 9)], VSXC (Van Voorhis-Scuseria exchange-correlation<sup>10</sup>), PBE0 (PBE with 25% exact exchange added<sup>11</sup>), PKZB (Perdew-Kurth-Zupan-Blaha<sup>12</sup>), B97 [Becke 1997 (Ref. 13)], B97-1 [Becke 1997 variant 1 (Ref. 14)], B97-2 [Becke 1997 variant 2 (Ref. 15)], the HCTH (Hamprecht-Cohen-Tozer-Handy) family,<sup>14,16,17</sup> OPTX/OPTC (optimized exchange/correlation<sup>18,19</sup>),  $\tau$ -HCTH and its hybrid,<sup>20</sup> TPSS (Tao-Perdew-Staroverov-Scuseria<sup>21</sup>), and B98 [Becke 1998 (Ref. 22)]. Two important avenues that have been pursued in this direction are (a) inclusion of new variables explicitly dependent on the Kohn-Sham orbitals, such as the kinetic energy density  $\tau$ , (b) treatment of DFT as a parametrized “semi-*ab initio*” method.<sup>23</sup>

In particular, the most commonly used hybrid functionals all involve parametrization against experimental data to some extent: For instance, the mixing parameters in B3LYP were fitted against the binding energies of the molecules in the G2-1 set.<sup>24</sup> Becke’s subsequent 1997 functional<sup>13</sup> involves a power series expansion in the reduced density gradient, parameters of which were fitted against the binding energies, ionization potentials, and proton affinities in the G2-1 set plus some additional data. An expansion of order  $m$  requires  $3m + 4$  parameters: for  $m = 4$  and higher the fit be-

came unphysical, and even  $m = 3$  appeared to exhibit signs of overfitting. Erring on the side of caution, Becke chose  $m = 2$ , involving ten parameters.

The issue of overfitting may be substantially alleviated by (a) admitting high-level *ab initio* data to the “training set;” (b) considering data other than energetics, such as gradients at the true equilibrium geometry (a convenient metric for geometry errors) and numerical exchange-correlation potentials extracted from high-level *ab initio* electron densities by means of the Zhao-Morrison-Parr<sup>25</sup> procedure. Tozer and Handy<sup>26–28</sup> followed this route, with only moderate success, as their functional form was “poorly chosen.”<sup>28</sup> Greater success was achieved by applying this more elaborate refinement procedure to Becke’s functional form, yielding the original HCTH/93 (Hamprecht-Cohen-Tozer-Handy<sup>14,29</sup>) functional. Besides this  $m = 4$  “pure DFT” functional, a reparametrization of Becke’s hybrid functional (denoted B97-1) was obtained as a byproduct.

The general performance of HCTH/93 was markedly superior to first-generation GGA (generalized gradient approximation) functionals such as BLYP (Becke-Lee-Yang-Parr<sup>3,6</sup>). However, it did not measure up to expectations for weakly bound systems;<sup>30,31</sup> in general, the absence of anions in the training set meant that the functional was not adequately parametrized for the outer regions of the electron density. In an attempt to remedy this problem and generally increase the versatility of the functional, it was reparametrized<sup>16,17</sup> to even larger sets of data including anions and weakly bound systems, culminating in the HCTH/407 functional.<sup>17</sup> The numerals in the notation refer to the number of chemical systems used in the training set.

Attempts to include additional variables such as the kinetic energy density  $\tau$  into the functional have been reviewed in the Introduction to Ref. 20. This latter paper represents an attempt to enhance HCTH with  $\tau$ -dependent terms. One intriguing question here is the actual role played by the kinetic energy density. Becke has argued<sup>32</sup> that local density functionals that include the kinetic energy density  $\tau$  can simulate delocalized exchange and thus, inclusion of  $\tau$  will improve

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generalized gradient functionals. Van Voorhis and Scuseria<sup>10</sup> presented evidence that such a form might be capable of simulating exact exchange. Boese and Handy<sup>20</sup> have similar experience, but conjectured that  $\tau$  does not merely simulate exact exchange, but rather *variable* exact exchange.<sup>20</sup>

This brings us to the subject of this paper. One well-known deficiency (see, e.g., Refs. 33 and 34) of most existing exchange-correlation functionals is their poor performance for reaction barrier heights: These are often significantly underestimated, and it is indeed not unusual for DFT not to find a barrier at all. Durant<sup>33</sup> noted that BH&HLYP (Becke half-and-half exchange with LYP correlation<sup>35</sup>), a hybrid functional with 50% exact exchange, was the exception to the rule in that it predicted transition state geometries and barriers reasonably well, despite being inferior to B3LYP (20% exact exchange) for thermochemical properties. Later, Truhlar and co-workers<sup>36</sup> and Kang and Musgrave<sup>37</sup> both proposed reparametrizations of existing functionals (modified Perdew-Wang<sup>9</sup> in the former, B3LYP without Becke exchange in the latter case) for barrier heights: both functionals involve a very high fraction of exact exchange, 42.7% in the case of mPW1K (modified Perdew-Wang for kinetics<sup>36</sup>), 55.7% in the case of KMLYP (Kang-Musgrave-Lee-Yang-Parr<sup>37</sup>). For both functionals, the improved performance for reaction barrier heights comes at the expense of seriously degraded performance for ground-state properties: in particular, errors in atomization energies and geometries exceed those for more conventional hybrid functionals with exact exchange in the 15%–25% range by a factor of 2–3.<sup>38</sup> In the case of KMLYP, an empirical G2-style “high-level correction” was proposed, but this is strictly a stop-gap solution as it will not affect properties other than equilibrium energetics.

For researchers involved in the computational study of reaction mechanisms (such as our own group, see, e.g., Refs. 39 and 40) the present situation is very frustrating—especially when a plethora of competing multistep pathways is to be considered<sup>39</sup>—as no single functional can be relied upon to get both relative stabilities and barrier heights right.

One possible route to such a functional might be variable exact exchange. If the kinetic energy density were truly capable of simulating variable exact exchange, however, then a fixed-exact exchange functional with  $\tau$ -dependent terms might afford a computationally much simpler solution. In the present paper, we will show that this is indeed the case, and shall propose a new general-purpose exchange-correlation functional to be known as BMK (Boese-Martin for kinetics).

Before discussing the development of the proposed functional, however, we would like to mention a couple of alternative approaches to tackling the aforementioned problem of transition states. These are connected to attempts by various groups at creating “third-generation functionals.” None of these functionals are currently accurate enough to replace any of the second-generation functionals.

Self-interaction-free or -corrected functionals constitute the first possibility. Here, an additional orbital-dependent correction is introduced,<sup>41</sup> causing the energy to lose invariance to rotations of occupied orbitals. Solving these equations self-consistently is both time consuming and difficult.<sup>42</sup>

Furthermore, no gradients or higher derivatives with respect to the geometry are available, which greatly reduces their usefulness in practical applications.

The second approach is to use functionals with so-called local exact exchange. However, such functionals either perform much less well when describing ground-state properties than the known functionals,<sup>43</sup> or have various difficulties describing spin splittings.<sup>44</sup>

## II. COMPUTATIONAL DETAILS

In order to obtain additional reference data beyond those in the HCTH/407 data set,<sup>17</sup> the W1 and W2 (Weizmann-1 and -2) computational thermochemistry protocols<sup>45,46</sup> were applied. Basically these methods represent approximations to the CCSD(T) (coupled cluster with iterative single and double, and quasiperturbative triple, substitutions<sup>93</sup>) infinite basis set limit: They generate average errors for total atomization energies (TAEs) in the kJ/mol range, and should therefore definitely be accurate enough for our purpose. The calculations were carried out by means of the MOLPRO 2002 electronic structure package<sup>47</sup> and a driver script written in Perl.<sup>48</sup>

A modified version of ACES II (Ref. 94) has been used to calculate UBD densities used in the developmental steps of the functional.

The parametrization of the functional itself was carried out using a collection of *ad hoc* programs and scripts written by one of us (A.D.B.): modified versions of both CADPAC (Ref. 49) and GAUSSIAN 03 (Ref. 50) were used as DFT engines.

Both are finite basis set DFT codes. The HCTH family of functionals was parametrized using a triple-zeta plus double polarization (TZ2P) basis set. We discovered early on in the present study that this basis set is insufficiently saturated for our purposes: we indeed found that in the case of the HCTH and  $\tau$ -HCTH functionals, some basis set superposition error has been absorbed into the functional. On the dependence of DFT parametrization on the basis set used, see Ref. 38. After some convergence studies, we decided on the following combination of basis sets: Jensen aug-pc2 (augmented polarization consistent-2) basis set<sup>51</sup> for {H, C, N, O, F}, TZ3P+diffuse (triple-zeta plus triple polarization plus diffuse, including an additional high-exponent *d* function as known to be required for many second-row compounds<sup>52</sup>) for {B, Al, Si, P, S, Cl}, the Wachters-Hay basis set<sup>53</sup> for first-row transition metals augmented with 2 *f* 1 *g* polarization functions taken from the Appendix to Ref. 54, the SDB-aug-cc-pVTZ basis set<sup>54</sup> for third- and fourth-row main group elements, and the 6-311+G(3*df*) basis set<sup>55</sup> for remaining elements. We are confident that this combination of basis sets is sufficiently close to the Kohn-Sham basis set limit for our purposes.

## III. TOWARDS A FUNCTIONAL FOR KINETICS

We shall try to develop a functional with the following design goals.

(1) Mean absolute error below 2 kcal/mol for reaction barrier heights.

(2) Smallest mean absolute error possible for atomization energies, geometry and harmonic frequencies of ground-state molecules.

(3) No separation between exchange and correlation functionals, in light of error cancellation between the two terms.

(4) A mathematically “simple” functional in order to facilitate insight.

(5) A power series expansion, yielding the maximum number of adjustable parameters (usually on the order of 10–20).

(6) A functional that obeys some of the more simple scaling conditions and furthermore is capable of modeling the exchange hole.<sup>22,56</sup>

(7) As diverse and balanced a parametrization set as possible, including transition metal (TM) complexes and hydrogen-bonded systems.

We will consider two different functional forms, one the hybrid HCTH (Ref. 14) form [of which B97 (Ref. 13) and B97-1 (Ref. 14) are special cases], the other the hybrid  $\tau$ -HCTH form. The exchange-correlation energy (with  $a$  as the mixing coefficient) is defined as

$$E_{XC} = E_{X,l} + E_{X,n-l} + E_C + aE_{HF}, \quad (1)$$

$$E_{X,l} = \sum_{\sigma} \int e_{X\sigma}^{LSDA}(\rho_{\sigma}) g_{X\sigma,l}(s_{\sigma}^2) d\mathbf{r}, \quad (2)$$

$$g_{X\sigma,l} = \sum_{i=0}^M c_{X\sigma,l,i} u_{X\sigma}^i, \quad (3)$$

$$E_{X,n-l} = \sum_{\sigma} \int e_{X\sigma}^{LSDA}(\rho_{\sigma}) g_{X\sigma,n-l}(s_{\sigma}^2) f_{X\sigma}(w_{\sigma}) d\mathbf{r}, \quad (4)$$

$$f_{X\sigma}(w_{\sigma}) = w_{\sigma} - 2(w_{\sigma})^3 + (w_{\sigma})^5, \quad (5)$$

$$w_{\sigma} = \frac{\frac{3}{5}(6\pi^2)^{2/3} \rho_{\sigma}^{5/3}}{\tau_{\sigma}} - 1, \quad (6)$$

$$g_{X\sigma,n-l} = \sum_{i=0}^M c_{X\sigma,n-l,i} u_{X\sigma}^i, \quad (7)$$

$$u_{X\sigma} = \gamma_{X\sigma} s_{\sigma}^2 (1 + \gamma_{X\sigma} s_{\sigma}^2)^{-1}, \quad (8)$$

$$E_C = \sum_{\sigma} E_{C\sigma\sigma} + E_{C\alpha\beta}, \quad (9)$$

$$E_{C\sigma\sigma} = \int e_{C\sigma\sigma}^{LSDA}(\rho_{\sigma}) g_{C\sigma\sigma}(s_{\sigma}^2) d\mathbf{r}, \quad (10)$$

$$g_{C\sigma\sigma} = \sum_{i=0}^M c_{C\sigma\sigma,i} u_{C\sigma\sigma}^i, \quad (11)$$

$$u_{C\sigma\sigma} = \gamma_{C\sigma\sigma} s_{\sigma}^2 (1 + \gamma_{C\sigma\sigma} s_{\sigma}^2)^{-1}, \quad (12)$$

$$E_{C\alpha\beta} = \int e_{C\alpha\beta}(\rho_{\alpha}, \rho_{\beta}) g_{C\alpha\beta}(s_{avg}^2) d\mathbf{r}, \quad (13)$$

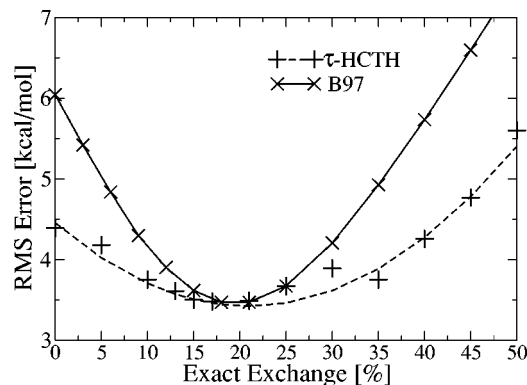


FIG. 1. Dependence on the exact exchange mixing coefficient of the rms error for the B97 and  $\tau$ -HCTH forms (energetic properties of the 147 set, kcal/mol).

$$g_{C\alpha\beta} = \sum_{i=0}^M c_{C\alpha\beta,i} u_{C\alpha\beta}^i, \quad (14)$$

$$u_{C\alpha\beta} = \gamma_{C\alpha\beta} s_{avg}^2 (1 + \gamma_{C\alpha\beta} s_{avg}^2)^{-1}. \quad (15)$$

Here,  $s$  is closely related to the reduced gradient

$$s_{\sigma}^2 = |\nabla \rho_{\sigma}|^2 \rho_{\sigma}^{-8/3}, \quad (16)$$

$$s_{avg}^2 = \frac{1}{2}(s_{\alpha}^2 + s_{\beta}^2). \quad (17)$$

The coefficients  $\gamma$  are nonlinear and fixed to

$$\gamma_{X\sigma} = 0.004, \quad (18)$$

$$\gamma_{C\sigma\sigma} = 0.2, \quad (19)$$

$$\gamma_{C\alpha\beta} = 0.006, \quad (20)$$

and the kinetic energy density  $\tau$  is defined as

$$\tau_{\sigma} = \sum (\nabla \phi_{i\sigma})^2. \quad (21)$$

For the B97 form,  $E_{X,n-l}$  will be zero. The B97-1 functional<sup>14</sup> has 12 linear coefficients with the sum over  $M$  in Eqs. (3), (11), and (13) going to  $M=2$ . The  $\tau$ -HCTH hybrid functional<sup>20</sup> had 16 linear coefficients with the sum over  $M$  in Eqs. (3), (7), (11), and (13) going to  $M=3$ . In both cases, the sum was truncated when no appreciable further improvement was seen from the inclusion of higher-order terms. The main improvement in the  $\tau$ -HCTH hybrid functional obviously came from the higher-order terms which included the kinetic energy density.

In a first “numerical experiment,” we varied the amount of Hartree-Fock exchange [the variable  $a$  in Eq. (1)] in each of these functionals in small increments between 0% and 50%, and “self-consistently” re-refined all other parameters to the HCTH/147 dataset<sup>17</sup> which is similar to the G2-2 dataset of Pople and co-workers.<sup>24,57,58</sup> The rms errors for both “metafunctionals,” as a function of the percentage of Hartree-Fock exchange, are plotted in Fig. 1.

We can make the following observations: First of all, both curves exhibit minima in the 20% range, consistent with experience. Second, the improvement afforded by the kinetic energy density terms is not nearly as large as one might have expected. Third, the main difference occurs far away from

TABLE I. W1 and W2 reaction barrier heights (kcal/mol) computed in this study, compared to experimental data (Ref. 59).

Reaction	Forward barrier			Reverse barrier		
	W1	W2	Expt.	W1	W2	Expt.
$C_5H_8 \rightarrow C_5H_8$	36.80		38.4	36.80		38.4
$C_2H_6 + NH \rightarrow C_2H_5 + NH_2$	19.35		18.4	9.86		8.0
$C_2H_6 + NH_2 \rightarrow C_2H_5 + NH_3$	11.25		10.4	17.93		17.8
$C_2H_6 + OH \rightarrow C_2H_5 + H_2O$	3.52		3.4	20.49		20.7
$CH_3 + H_2 \rightarrow CH_4 + H$	11.89	11.89	12.1	14.88	14.92	15.0
$CH_3 + OH \rightarrow CH_4 + O$	9.00		7.8	14.28		13.7
$CH_4 + NH \rightarrow CH_3 + NH_2$	21.98		22.7	8.95		8.4
$CH_4 + NH_2 \rightarrow CH_3 + NH_3$	13.92		15.5	16.97		17.9
$CH_4 + OH \rightarrow CH_3 + H_2O$	6.22		6.7	19.66		20.2
$H_2 + Cl \rightarrow H + HCl$	6.97	7.90	8.7	5.62	4.98	5.6
$H_2 + F \rightarrow H + HF$	a		1.8			33.2
$H_2 + OH \rightarrow H + H_2O$	5.29	5.40	5.7	21.72	21.65	22.0
$H_2S + H \rightarrow SH + H_2$	3.45	3.62	3.6	17.01	17.14	17.4
$H_2 + H \rightarrow H + H_2$	9.60	9.66	9.6	9.60	9.66	9.6
$CH_3OH + H \rightarrow CH_2OH + H_2$	9.64		7.3	15.70		13.8
$CH_3 + HCl \rightarrow CH_4 + Cl$	1.37		1.8	7.39		7.8
$HCl + H \rightarrow H + HCl$	17.21	17.25	18.0	17.21	17.25	18.0
$N_2H_2 + H \rightarrow N_2H + H_2$	2.90	2.81	5.9	40.48	40.64	41.0
$PH_3 + H \rightarrow PH_2 + H_2$	2.58	2.78	3.2	24.58	24.75	25.5
$NH_3 + OH \rightarrow NH_2 + H_2O$	3.54		3.2	13.92		13.2
$OH + Cl \rightarrow O + HCl$	b		9.8			9.9
$OH + H \rightarrow O + H_2$	10.96	10.94	10.1	13.25	13.48	13.1

<sup>a</sup>CCSD(T) of doubtful value due to severe nondynamical correlation. Value of 2.31 kcal/mol taken from benchmark calculation by Kállay *et al.* (Ref. 61).

<sup>b</sup>CCSD(T) of doubtful value due to severe nondynamical correlation. Experimental value used (see text).

the minimum: the metafunctional including  $\tau$  deteriorates much less rapidly than the one without, both as exact exchange is reduced to zero and as it is cranked up into the 50% region.

It may be instructive to consider the evolution of the parameters—particularly the zeroth-order linear coefficients of Eqs. (3)–(14) which contribute most to the energy—as a function of “exact exchange” admixture. All these coefficients, save the second nonlocal one, will be unity for the uniform electron gas. For the B97-like form, the zeroth-order exchange coefficient  $c_{X\sigma,1,0}$  varies from 1.1 (at 0% HF exchange) to about 0.4 (at 50% HF exchange). For the  $\tau$ -HCTH-like form, at 50% exact exchange mixing, this coefficient stands at 0.5, or 1.2 higher than without the terms including the kinetic energy density. As we would have expected, the  $c_{X\sigma,n-1,0}$  coefficient changes from near zero (0.001) at 0% HF exchange to  $-0.38$  at 50% HF exchange. Hence, the terms including the kinetic energy become much larger, apparently “correcting back” the exact exchange mixing. Furthermore, the zeroth-order correlation coefficients are greatly affected by adding exact exchange: For example,  $c_{C\sigma\sigma,0}$  actually becomes negative. For the B97 form, these coefficients change from 0.4 to  $-2.8$ . The  $\tau$ -HCTH form, however, behaves completely differently, with  $c_{X\sigma\sigma,0}$  remaining around 0.4. For the B97 form, this effect is canceled by the  $c_{X\alpha\beta,0}$  coefficient, going from 0.5 to 1.8. Again, the  $\tau$ -HCTH form functionals coefficient does barely change from 0.7 to 0.9. As a conclusion, we note that the terms depending on the kinetic energy density have to be responsible for the relatively shallow “ $\tau$ -including” curve in Fig. 1. Moreover, changes in the coefficients are by and large lim-

ited to the exchange part, while for the  $\tau$ -free (B97) form, both exchange and correlation coefficients are quite sensitive to variation in the amount of Hartree-Fock exchange. Thus, in short, introduction of Eqs. (4) and (5) into the functional makes it capable of correcting *back* for excess exact exchange.

This immediately begs the question whether this property of the  $\tau$ -HCTH hybrid form also applies to reaction barrier heights and transition state geometries. Furthermore, what would be the behavior of the various terms and parameters as a function of the percentage of Hartree-Fock exchange?

For this purpose, we included such transition states into our “training” or “fitting” set. At this stage, we employed the set of reactions proposed by Truhlar and co-workers<sup>59</sup> for which accurate experimentally derived barrier heights (including tunneling and other quantum corrections) are available. To this we added two identity  $S_N2$  reactions for which accurate barriers were previously determined by W2 theory.<sup>60</sup> For Truhlar’s reactions, we performed W1 and W2 reference calculations at the QCISD/MG3 (quadratic configuration interaction<sup>95</sup>) geometries given in the Supporting Information to Ref. 59. Results are summarized in Table I. Overall, the agreement between theory and the values derived from experiment is quite good: any discrepancies would be primarily due to post-CCSD(T) correlation effects, or uncertainty in the measurements or quantum corrections. The transition states of the reactions  $H_2 + F$  and  $OH + Cl$  exhibit severe nondynamical correlation, and CCSD(T) data would not be very meaningful. In the case of the  $H_2 + F$  reaction, we prefer to use the barrier of 2.31 kcal/mol ob-

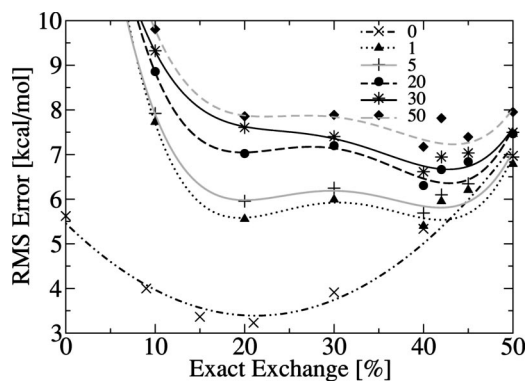


FIG. 2. Dependence on the exact exchange mixing coefficient, and the weight assigned to reaction barrier heights in the parametrization, of the rms error for the B97 form (energetic properties of the 147 set, kcal/mol).

tained by Kállay *et al.*<sup>61</sup> in the set, and in the case of the OH+Cl reaction, we ended up employing the experimental value of 9.8 kcal/mol. Altogether 44 barriers (22 forward and 22 reverse) are reported in Table I, although obviously, a method that would get both the forward barrier and the reaction energy right would automatically give the right answer for the reverse barrier—so either the reverse barrier height or the reaction energy would be redundant data. For determining the functional, we included these 22 forward reaction barrier heights plus the reaction barriers of  $\text{Cl} + \text{CH}_3\text{Cl} \rightarrow \text{Cl} + \text{CH}_3\text{Cl}$  and  $\text{F} + \text{CH}_3\text{F} \rightarrow \text{F} + \text{CH}_3\text{F}$ . Since only some of the molecules in Table I were included in the HCTH/147 set, we only use 14 of the 19 reaction energies in the small set. These were augmented with nine reaction energies<sup>62</sup> that were used by Schütz *et al.* to assess local correlation methods.<sup>63</sup>

If we were to exclusively consider errors in atomization energies, it is at least in principle possible that just a particular type of bond is poorly described, and the error statistics obtained are not representative for reactions involving formation and/or breaking of other bond types. Adding reaction energies to the training set at least allows us to verify that the various molecules involved at least yield correct energetics relative to their molecular “next of kin.” Furthermore, typical DFT studies are probably more likely to focus on reaction energies than on atomization energies.

The original HCTH/147 set<sup>16</sup> was thus enlarged by 22 reaction barrier heights, 23 reaction energies, the dissociation energy of the  $\text{NH}_3$  and  $(\text{H}_2\text{O})(\text{NH}_3)$  dimers, and some potential energy points of the  $\text{NH}_3$  dimer surface.<sup>64</sup> The latter two properties were given low weights, while the reaction energies were assigned ten times the weight for the atomization energies, thus taking into account that said reaction energies are an order of magnitude smaller than typical atomization energies multiplied by the molecularity (number of molecules involved) of the reaction.

Once again, all parameters were self-consistently refitted for every value of the exact exchange coefficient, and this analysis was repeated for various relative weights assigned to the barrier heights in the “penalty function.” For the  $\tau$ -free form, profiles of the rms errors for all energetics other than barrier heights are plotted in Fig. 2 (every curve representing

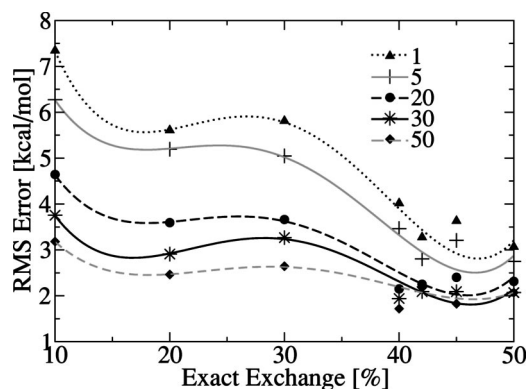


FIG. 3. rms error (kcal/mol) for barrier heights with the B97 form as a function of the exact exchange admixture and the weight assigned to barrier heights in the parametrization.

a different weight factor for the barrier heights), while the corresponding profiles for the barrier heights themselves can be found in Fig. 3. With a zero weight for the transition states, the expected single minimum around 20% Hartree-Fock exchange is obtained. However, as soon as the barriers are even given a unit weight, a second minimum appears around 40%. As the weight for the transition states is increased, both minima persist at least through  $W_{\text{TS}}=50$ . Note that the curves are not perfectly smooth since the final parameters are somewhat dependent on the initial parametrization chosen.

For a functional to be useful for transition states, barriers have to be predicted quite accurately—especially for reactions with low barriers which might otherwise be spuriously rendered barrierless. A 2 kcal/mol rms target accuracy would, according to Fig. 3, require  $W_{\text{TS}}=50$ . Using this relative weight, we have plotted rms error profiles for both barrier heights and other energetic properties as a function of the percentage of Hartree-Fock exchange in Fig. 4, for both the  $\tau$ -free and the  $\tau$ -including forms. Parameter optimizations for the latter took the final parameters for the former as initial guesses.

Note that the minimum around 20% for the nonbarrier energetics is now very shallow, and that both functional forms exhibit a deeper second minimum around 40%. For

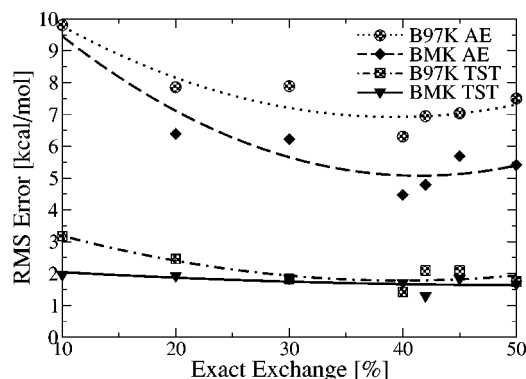


FIG. 4. rms errors (kcal/mol) of the B97 and  $\tau$ -HCTH forms for the extended 147 set and for barrier heights as a function of the exact exchange admixture and the weight assigned to barrier heights in the parametrization.

TABLE II. Coefficients of the proposed functionals, where both functionals have 42% exact exchange. In addition, the B97 and  $\tau$ -HCTH functionals when just fitting them to the 147 set (without transition states) are shown for comparison.

Functional fitted to	Transition states+ energies		Energies	
	B97-K	BMK	B97-K like	BMK-type
Exact exchange mixing	42%		45%	
$c_1 = c_{X\sigma,local,0}$	0.507 863	0.474 302	0.454 579	0.554 540
$c_2 = c_{X\sigma,nonlocal,0}$		-0.192 212		-0.808 213
$c_3 = c_{C\sigma\sigma,0}$	0.123 55	-2.190 98	-2.515 95	0.452 26
$c_4 = c_{C\alpha\beta,0}$	1.586 13	1.223 34	1.681 37	0.892 43
$c_5 = c_{X\sigma,local,1}$	1.468 73	2.777 01	1.700 57	0.115 65
$c_6 = c_{X\sigma,nonlocal,1}$		4.739 36		0.686 19
$c_7 = c_{C\sigma\sigma,1}$	2.653 99	23.893 9	12.899 7	-9.175 79
$c_8 = c_{C\alpha\beta,1}$	-6.209 77	-3.463 1	-8.996 6	6.476 24
$c_9 = c_{X\sigma,local,2}$	-1.513 01	-11.423 0	-2.274 1	-0.320 78
$c_{10} = c_{X\sigma,nonlocal,2}$		-26.618 8		-16.039 9
$c_{11} = c_{C\sigma\sigma,2}$	-3.206 94	-44.330 3	-11.084 0	27.666 5
$c_{12} = c_{C\alpha\beta,2}$	6.461 06	10.073 1	12.650 2	-36.963 2
$c_{13} = c_{X\sigma,local,3}$		11.716 7		-0.640 2
$c_{14} = c_{X\sigma,nonlocal,3}$		22.489 1		-5.775 5
$c_{15} = c_{X\sigma\sigma,3}$		22.598 2		-19.903 5
$c_{16} = c_{X\alpha\beta,3}$		-11.197 4		31.878 8

the barrier heights, there only appears to be a single minimum, at 42% to be precise.<sup>65</sup> This value was retained for the final functionals.

The B97-1 like  $\tau$ -less form was frozen at this stage, and will henceforth be denoted B97-K (Becke-97 for “kinetics”).

The  $\tau$ -dependent form was then subjected to its final refinement. On the one hand, we expanded the training set to an enlarged version of the HCTH/407 set,<sup>17</sup> encompassing 464 energetic properties and 4008 cartesian gradient components. This set includes nearly the full G3-99 set of molecules<sup>66</sup> minus some very large organic systems, plus several dissociation energies of hydrogen-bonded complexes and stationary points on the ammonia dimer potential surface taken from Ref. 64, and several ligand dissociation energies of transition metal complexes—in addition to the reaction barrier heights already discussed. On the other hand, we replaced TZ2P by the large basis set described in Sec. II. Full details of all the data are available in the Supplementary Material.<sup>67</sup>

The final functional thus obtained is denoted BMK (from the present authors’ initials and the K of kinetics). The parameters of both B97-K and BMK are given in Table II. Some of their values are somewhat surprising if we consider the coefficients of these functionals when no barrier heights are included, as discussed above. We will first discuss the GGA (B97) functional form. With a larger fraction of exact exchange, the zero-order correlation coefficients  $c_{C\sigma\sigma,0}$  and  $c_{C\alpha\beta,0}$  will try to correct back the large amount of exchange mixing, together with a smaller local exchange coefficient  $c_{X\sigma,local,0}$ . Introducing transition states into the fit to obtain B97-K will reverse this effect, since this large amount of exact exchange is needed.

The  $\tau$ -HCTH form, however, behaves *the opposite way*. Here, with a larger fraction of exact exchange, the nonlocal exchange coefficients can now correct back the exchange,

yielding positive correlation coefficients  $c_{C\sigma\sigma,0}$  and  $c_{C\alpha\beta,0}$ .

When introducing the transition states into the set to obtain BMK, these nonlocal coefficients are now needed for something else, and the zero-order correlation and exchange coefficients look similar to the B97 functional with a larger fraction of exact exchange. While having a small effect on the other coefficients at the minimum in Fig. 1 (see Table II of Ref. 20 for comparison), the kinetic energy density has a *very large* effect as soon as the amount of exact exchange is not around 15%–25%. This explains the previously reported observation that functionals employing the kinetic energy density are capable of simulating exact exchange. It also implies that with large values of the exact exchange mixing coefficient, the benefits derived from incorporating the kinetic energy density and similar variables into DFT functionals will be even larger.

We shall now finally assess the proposed functionals for a variety of properties, in particular as to how they measure up compared to other functionals designed either specifically for barrier heights or for equilibrium energetics.

#### IV. ASSESSMENT OF DENSITY FUNCTIONALS

As our final parametrization set of 464 systems is larger and arguably more diverse than any previously used, we shall use it for comparison with other functionals as well. We have considered (a) the GGA functionals BP86 (Becke exchange<sup>3</sup> with Perdew 1986 correlation<sup>4</sup>), BLYP (Refs. 3 and 6), HCTH/407 (Ref. 17), and PBE (Perdew-Burke-Ernzerhof<sup>8</sup>); (b) the meta-GGA functionals  $\tau$ -HCTH (Ref. 20) and VSXC (Ref. 10); (c) the hybrid functionals B3LYP (Refs. 6 and 7) B97-1 (Ref. 14), B97-2 (Ref. 68), PBE0 (Refs. 8 and 11),  $\tau$ -HCTH hybrid,<sup>20</sup> KMLYP (Ref. 37) and mPW1K (Ref. 36). We employed the same large *spdf* basis set for the assessment as was used for the final

TABLE III. rms energy errors for the proposed functionals, compared with BP86, BLYP, HCTH/407, PBE,  $\tau$ -HCTH, VSXC, B3LYP, B97-1, B97-2, PBE0,  $\tau$ -HCTH hybrid, KMLYP, and mPW1K. All errors in kcal/mol, except ionization potentials (eV), electron affinities (eV), and sum of gradient components (a.u.) at their reference (experimental/theoretical) equilibrium geometry.

Class	HCTH				$\tau$			$\tau$				mPW1K	B97-K	BMK	
	BP86	BLYP	/407	PBE	HCTH	VSXC	B3LYP	B97-1	B97-2	PBE0	HCTHh				KMLYP
All systems (404)	21.2	10.3	7.9	18.9	7.1	7.8	7.7	5.3	5.3	9.3	5.5	25.6 <sup>a</sup>	14.0	10.3	5.6
Neutrals (219)	21.8	11.6	8.6	21.3	7.6	6.8	8.1	4.8	4.6	8.5	5.1	27.7 <sup>a</sup>	15.8	11.5	4.5
Anions (58)	15.2	9.5	7.8	13.4	6.4	10.3	9.1	6.3	6.1	9.7	6.3	20.9 <sup>a</sup>	13.9	10.8	7.9
Cations (88)	15.1	8.3	7.0	18.8	6.3	9.3	5.7	5.5	5.6	11.8	5.6	27.7 <sup>a</sup>	10.2	7.0	6.6
TM complexes (5)	11.1	4.2	4.7	13.3	4.1	5.5	17.0	13.1	15.2	14.3	7.2	29.0 <sup>a</sup>	28.7	25.0	10.8
TSes (24)	10.1	8.5	7.0	10.3	7.9	6.2	5.0	5.2	4.1	4.9	6.1	3.2	1.8	2.0	2.0
Reaction energies (62)	5.0	6.4	5.7	5.3	4.6	6.8	4.4	4.2	3.4	4.3	4.0	8.2 <sup>a</sup>	4.8	4.4	3.7
IPs (80)	0.23	0.28	0.25	0.24	0.23	0.24	0.23	0.22	0.21	0.23	0.22	0.41 <sup>a</sup>	0.27	0.27	0.24
EAs (58)	0.22	0.18	0.24	0.19	0.18	0.18	0.19	0.16	0.18	0.20	0.17	0.27 <sup>a</sup>	0.26	0.22	0.19
$\Sigma\Delta$ gradient (4008)	17.52	19.01	12.10	16.84	11.56	10.96	11.17	10.72	11.80	12.33	10.77	30.71	20.24	11.61	13.53

<sup>a</sup>Exclusive of high-level correction from Ref. 37.

parametrization cycles of BMK. Summary error statistics for all functionals, broken down by type of molecule or property, are presented in Table III.

For the nonhybrid functionals, the results of the previous investigations with the TZ2P and cc-pVTZ basis sets<sup>38</sup> are corroborated: For all molecules, the  $\tau$ -HCTH functional yields the lowest errors, followed by the HCTH/407 and VSXC functionals. Particularly BP86 and PBE yield very large errors when considering geometries and atomization energies. Interestingly, this pattern is not necessarily carried over from the TAEs to the reaction energies: for instance, VSXC has half the rms error for atomization energies of BLYP but both functionals perform similarly (somewhat poorly) for reaction energies. As to the geometry gradient errors which correlate with geometry errors (see also Refs. 17 and 20), the best performance appears to be put in by those functionals that perform best for TAEs (i.e., the meta-GGAs and HCTH/407).

HCTH/407 and both meta-GGA functionals in fact are overall competitive with the very popular B3LYP hybrid functional, in turn surpassed by B97-1 and B97-2. Interestingly (although perhaps fortuitously), all hybrid functionals perform worse than the (meta-)GGAs for transition metal ligation energies, although this problem is greatly mitigated in  $\tau$ -HCTH hybrid. For our dataset, the best hybrid functionals (B97-1 and B97-2) overall represent an improvement over (meta-)GGAs for TAEs, but not significantly so for ionization potentials and electron affinities. As expected, the transition state optimized mPW1K and KMLYP functionals perform rather poorly for the thermochemical properties, although this would be mitigated somewhat in the case of KMLYP by applying their recommended high-level additive correction. For geometric parameters, the rms error of mPW1K is twice, and that of KMLYP thrice, that of other functionals. Interestingly, mPW1K performs reasonably well for the reaction energies.

Our B97-K functional fares better than mPW1K, with errors for equilibrium energetics generally in between mPW1K and B97-1, and errors for geometries comparable to B3LYP or  $\tau$ -HCTH hybrid (cut in half compared to mPW1K). But it is for BMK that performance is particularly

pleasing: its performance for most energetic properties is comparable to the best hybrid general-purpose functionals, despite its high percentage of Hartree-Fock exchange. Indeed, for transition metal complexes it has the second best performance of all hybrid functionals, after  $\tau$ -HCTH hybrid. For geometries, its rms error is somewhat deteriorated compared to B97-1 or to its closest kin,  $\tau$ -HCTH hybrid, but still much lesser than that of mPW1K or KMLYP. The performance of BMK for TAEs of neutral molecules is especially pleasing. Error statistics for ionization potentials and electron affinities are comparable to B3LYP. Overall, BMK can hold its own with general-purpose hybrid functionals for equilibrium energetics and geometries.

Interestingly, the improvements previously reported<sup>20</sup> for the  $\tau$ -HCTH hybrid functional compared to B97-1 now vanish because of the larger basis set (compared to TZ2P used in the earlier work). This suggests again that some basis set incompleteness error may have been absorbed in the parametrization of the HCTH family.<sup>69</sup>

For reaction barrier heights, the general-purpose hybrid functionals represent an improvement over all (meta-)GGAs except perhaps  $\tau$ -HCTH. Yet they are clearly trumped by the transition state-optimized functionals, three of which (mPW1K, B97-K, and BMK) have errors around 2 kcal/mol.

Histograms of the errors for the BMK and B97-K functional, as well as for B3LYP and mPW1K, are given in Figs. S-1 through S-4 in the Electronic Supplement to this paper.<sup>70</sup> The error distributions can be fitted rather well (correlation coefficients  $R$  ranging from 0.98 for B97-K to 0.993 for BMK) by a normal distribution  $A \exp(-(x-\mu)^2/2\sigma^2)$ , which has been displayed in each graph together with its mean  $\mu$  and standard deviation  $\sigma$ . We can see that we did not merely remedy an additive bias (with  $\mu$  shifting from  $-4.1$  kcal/mol for mPW1K to  $-0.6$  kcal/mol for BMK), but that the error distribution was narrowed by a factor of 2 (from  $\sigma=6.7$  kcal/mol for mPW1K to 3.3 kcal/mol for BMK), and that BMK indeed compares favorably to B3LYP ( $\mu=-1.4$ ,  $\sigma=4.3$  kcal/mol) in both respects. In contrast, B97-K only represents a minor improvement ( $\mu=-3.9$ ,  $\sigma=6.4$  kcal/mol) over mPW1K.

Overall, BMK turns in a very strong performance in

TABLE IV. Harmonic frequency errors ( $\text{cm}^{-1}$ ) for a variety of functionals.

Functional	Mean error	Mean absolute error	rms error
BP86	-57.6	58.9	79.1
BLYP	-61.5	62.2	83.9
HCTH/407	-27.8	35.4	52.0
PBE	-54.0	55.9	75.0
B3LYP	-2.7	21.6	30.8
B97-1	-2.5	18.3	26.3
B97-2	12.6	22.9	32.8
PBE0	12.5	23.9	34.8
KMLYP	86.3	87.0	104.6
mPW1K	57.6	58.0	72.6
B97-K	28.4	30.2	40.7
BMK	27.3	31.7	45.9

Table III, with energy errors in close proximity to hybrid functionals that employ a much smaller fraction of exact exchange (15%–25%). The gradient and thus geometry errors are somewhat larger, and probably in the range of a good meta-GGA or GGA functional such as HCTH/407.

Another important indication of the reliability of the functionals are frequency calculations. These are especially important in order to find out if a functional has been “overfitted.” In this instance, the gradients would become quite small and achieve a small gradient error for the wrong reason: The gradients at *any* geometry would be small, even if comparatively far away from equilibrium. This would result in a flattened potential energy surface and thus in too low frequencies.<sup>71</sup> In order to ensure a balanced evaluation set (including organic molecules) and reliable data, we have mainly used CCSD(T)/cc-pVQZ, CCSD(T)/aug-cc-pVQZ, and CCSD(T)/ANO4321 harmonic frequencies from the literature [we may assume that these values are quite accurate because of known error cancellation<sup>72</sup> between core-correlation and post-CCSD(T) correlation effects].<sup>73–85</sup> Using these reference values, we included the following molecules:  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_6\text{H}_6$ ,  $\text{CCl}_2$ ,  $\text{CF}_2$ ,  $\text{CF}_4$ ,  $\text{CH}_2\text{NH}$ ,  $\text{CH}_4$ ,  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{F}_2$ ,  $\text{FCCH}$ ,  $\text{H}_2$ ,  $\text{H}_2\text{CO}$ ,  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{SiO}$ ,  $\text{HCN}$ ,  $\text{HF}$ , *cis*-HSiOH, *trans*-HSiOH,  $\text{N}_2$ , *cis*- $\text{N}_2\text{H}_2$ , *iso*- $\text{N}_2\text{H}_2$ , *trans*- $\text{N}_2\text{H}_2$ ,  $\text{N}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{SiH}_4$ ,  $\text{SiF}_4$ ,  $\text{SO}_2$ ,  $\text{SO}_3$ , and *s*-tetrazine. This makes for a total of 202 distinct harmonic frequencies: all computed values are given in the Supplementary Material,<sup>67</sup> while mean signed, mean absolute, and rms errors over the whole set are displayed in Table IV. We investigated the performance of the BP86, BLYP, HCTH/407, and PBE GGA functionals, together with B3LYP, B97-1, B97-2, PBE0, KMLYP, mPW1K, B97-K, and BMK. For technical reasons, the BMK frequencies have been calculated by numerical differentiation of gradients. For the harmonic frequencies investigated, GGA functionals generally underestimate, and hybrid functionals with large fractions of exact exchange overestimate, the coupled-cluster values. Among the GGA functionals, HCTH/407 clearly yields the lowest errors, underestimating the frequencies by an average  $30 \text{ cm}^{-1}$ . There is little difference between the hybrid functionals B3LYP, B97-1, B97-2, and PBE0, with an improvement of 17% by B97-1 compared to B3LYP. Our investigations<sup>85</sup> indicate that this improvement for B97-1 largely derives from organic molecules, which are described

TABLE V. Reference values for the ten hydrogen-bonded complexes. Dissociation energies by W2 theory; geometry shifts CCSD(T)/aug'-cc-pVQZ; frequency shifts MP2/aug'-cc-pVQZ. aug'-cc-pVQZ stands for cc-pVQZ on hydrogen and aug-cc-pVQZ on all other elements.

Dimer	$D_e$ (kJ/mol)	Donor $\Delta r_{XH}$ (Å)	H-bond length (Å)	Frequency shift ( $\text{cm}^{-1}$ )
(ClH)(NH <sub>3</sub> )	34.9	0.0434	1.79	-770
(CO)(HF)	7.1	0.0018	2.07	-32
(FH)(NH <sub>3</sub> )	52.1	0.0317	1.70	-785
(H <sub>2</sub> O) <sub>2</sub>	20.8	0.0063	1.95	-170
(H <sub>2</sub> O)(NH <sub>3</sub> )	26.8	0.0117	1.98	-298
(H <sub>3</sub> O)(H <sub>2</sub> O) <sup>+a</sup>	141.2	0.2366	1.19	-2780
(HCl) <sub>2</sub>	8.4	0.0039	2.56	-72
(HF) <sub>2</sub>	19.1	0.0057	1.82	-138
(OC)(HF)	14.8	0.0061	2.08	-172
(NH <sub>3</sub> ) <sub>2</sub>	13.2	0.0033	2.30	-134

<sup>a</sup>Symmetric structure with central H atom, better written as  $\text{H}_5\text{O}_2^+$ .

even better than with B3LYP. Generally, the geometry gradient errors in Table III seem to transfer rather well into frequency errors for these functionals, with B97-K and BMK yielding errors comparable to a functional like HCTH/407. Again, KMLYP and mPW1K yield frequency errors as bad as, or even worse than, GGA functionals.

Hydrogen-bonded complexes serve as another commonly used test for density functionals. *Ab initio* calculations on such systems converge quite rapidly with the electron correlation treatment (thanks to the long-range character of the interaction studied) but very slowly with the basis set,<sup>86</sup> both with and without counterpoise<sup>87</sup> corrections. Since the use of extrapolation schemes almost eliminates the basis set superposition errors for atomization energies<sup>88</sup> and hydrogen-bonded complexes such as the ammonia dimer,<sup>64</sup> it is safe to assume that use of standard W2 theory<sup>45</sup> will suffice. Further touchstones for hydrogen-bonded complexes include the lengths of the hydrogen bonds and hydrogen-bonded shifts calculated using CCSD(T)/aug'-cc-pVTZ. The harmonic frequency shifts are obtained at the MP2/aug'-cc-pVTZ level. We have computed reference values for nine hydrogen-bonded complexes which were also used in a previous study,<sup>30</sup> in addition to the ammonia dimer. All these values (Table V), with the exception of the MP2 frequency shifts (for which we would expect a deviation of about 15%), should be very accurate. In Table VI, the mean% and rms % errors are defined by

$$\text{mean} = \frac{1}{10} \sum_i^n \left( \frac{\text{value}(\text{complex}(i))}{\text{value}(\text{reference}(i))} - 1 \right) \times 100\%$$

and

$$\text{rms} = \sqrt{\frac{1}{10} \sum_i^n \left( \frac{\text{value}(\text{complex}(i))}{\text{value}(\text{reference}(i))} - 1 \right)^2} \times 100\%.$$

In this Table, all interaction energies (MP2/a'pVQZ and DFT/aug-TZ) have been counterpoise corrected. For the DFT and MP2 methods tested, counterpoise corrections are generally on the order of about 0.5–2.0 kJ/mol, which is sometimes still quite large relative to the interaction energies being considered. For the reference W2 values, *all* residual



TABLE VI. Relative errors of the functionals and MP2/aug'-cc-pVQZ for the hydrogen-bonded complexes.

Functional	Dissociation energy		$\Delta r$ (H-bond)		$\Delta r$ (H-bond)		Frequency shift	
	Mean%	rms%	Mean%	rms%	Mean%	rms%	Mean%	rms%
BP86	-12.5	25.3	80.9	91.2	-2.87	4.20	40.3	49.9
BLYP	-14.6	21.6	42.7	46.8	-1.01	1.97	16.9	30.2
HCTH/407	-7.5	9.0	-2.7	26.3	4.28	5.88	-14.1	23.3
PBE	8.6	14.0	76.9	86.0	-3.30	4.54	40.1	49.3
B3LYP	-8.5	15.0	29.0	31.3	-0.39	1.32	9.1	16.3
B97-1	3.0	6.0	33.4	38.2	-1.01	2.07	11.4	16.2
B97-2	-19.6	25.3	18.9	25.0	1.08	2.96	4.4	8.5
PBE0	2.3	9.4	46.1	52.8	-2.46	3.26	24.0	29.3
KMLYP	32.2	34.5	51.4	57.6	-5.38	5.66	33.0	46.0
mPW1K	-38.0	40.9	-32.1	36.3	9.67	10.55	-32.9	40.0
B97-K	-1.7	6.7	2.8	6.0	1.26	1.40	-9.2	13.0
BMK	-17.8	24.8	32.4	37.9	-0.68	1.50	4.5	25.2
MP2	-1.8	8.0	15.2	19.6	-0.33	1.47	(0.0)	(0.0)

basis set superposition error (BSSE) is likely to have been eliminated. Thus, we would expect the mean error to change by +2%–3%, so that the mean percentual error of MP2 in Table V will be approximately zero, and the functionals *underestimating* the interaction energy (like HCTH/407 and B3LYP) will become more accurate. All the computed values can be found in the Supplementary Material.<sup>67</sup> Generally, it is believed that MP2 renders much more accurate results than density functional theory for hydrogen-bonded systems. Overall, the *consistency* of results of MP2 is only matched by one functional, surprisingly B97-K. The errors of this functional are low for all tested properties, from the dissociation energy to the frequency shift of the hydrogen bond. BMK, on the other hand, renders a mediocre performance, which looks quite similar to the B97-2 functional. Concerning the dissociation energies, HCTH/407 is the only functional giving a rms% error of less than 10. Only the hydrogen-bond distance itself is consistently overestimated by about 4%. The same is true for B97-1: For all properties investigated it yields low errors, except for the geometry shift. Generally, hybrid functionals are more accurate than GGA functionals (with HCTH/407 yielding particularly good dissociation energies and BLYP hydrogen bond lengths), which are in turn much more accurate than the other two kinetics functionals investigated. mPW1K shows the behavior we would expect from the HF method, i.e., underestimating the interaction energy, the hydrogen and frequency shifts by about 40%, and overestimating the bond length. KMLYP on the other hand shows some behavior normally associated with a functional fit to the uniform electron gas, such as LSDA: The interaction energy and the shifts are overestimated and the bond length underestimated. Overall, the proposed functionals show much improved performance for hydrogen-bonded complexes, with B97-K, surprisingly, clearly yielding the lowest error of all functionals tested.

Finally, we will consider performance of BMK and other functionals for transition states outside our training set. Unlike for the latter, all transition states will be optimized with the functional and basis set used. The results are presented in detail in Table S-1 in the Electronic Supplement.<sup>70</sup> summary error statistics can be found in Table VII. The source of the

reference values was indicated in the second column of Table S-1. Entries 1–24 are the reactions from the training set. The remainder are a large subset of the reactions considered by Kang and Musgrave in the KMLYP paper,<sup>37</sup> and finally the reactions from the recent paper of Houk and co-workers<sup>89</sup> on pericyclic reactions like ring closings, hydrogen shifts, and Diels-Alder reactions. For this class of reactions, Houk and co-workers found average errors ranging from 1.7 to 3.2 kcal/mol for several hybrid functionals. It should be noted that the average uncertainty of the experimental values is itself 0.7 kcal/mol, casting some doubt on the validity of overly detailed comparisons for these systems. In one case (the ring closing of 1,3-butadiene to cyclobutene), the 0.2 kcal/mol stated uncertainty appears to be somewhat optimistic: our computed W1 barrier deviates by 1.8 kcal/mol—changing by at most 0.1 kcal/mol when computed at different calculated reference geometries—despite the absence of significant nondynamical correlation. The other reactions we investigated where the hydrogen shifts of 1,3-cyclopentadiene and 1,3-pentadiene, and the ring closing of ethylene and 1,3-butadiene to cyclohexene. In all cases the results suggest that the experimental values might have larger deviations than their given uncertainties: For the first we found a difference of 2.2 kcal/mol (which is close to their CBS-GB3 number reported), compared to the stated uncertainty of 0.5 kcal/mol. For the second, the W1 result is somewhat closer to experiment with a deviation of 0.7 kcal/mol, the reported uncertainty being 0.5 kcal/mol. For the third, the W1 value is 1 kcal/mol higher than the reported experimental value. In all four cases, the reported experimental values are lower than our W1 data, and BMK agrees more closely with the latter.

In addition, the experimental numbers of Kang and Musgrave (marked with footnote symbol a) deviate significantly from the ones reported by Truhlar and co-workers for reactions 19–24. This casts some doubt on the accuracy of the former: However, for want of other data for many reactions, we will still use this set for comparison.

In Table S-1, we have tested mPW1K, KMLYP, B3LYP, B97-1, and B97-2 together with the two newly obtained density functionals and the *spdf* basis set combination de-

TABLE VII. Error statistics of the functionals for the various sets of barrier heights in Table S-1. Set 1 consists of the reactions from Table I; set 2 are some anionic  $S_N2$  reactions taken from Ref. 60; set 3 was taken from Kang and Musgrave (Ref. 37); the pericyclic organic reactions from the work of Houk and co-workers (Ref. 89) constitute set 4.

Set	Set specifications			Method							
	Reference	# TSs	Error	BMK	B97-K	mPW1K	KMLYP	B3LYP	B97-1	B97-2	G2
1,2	W1/W2, Expt.	24	Mean	-0.8	-0.3	-0.7	-2.4	-4.1	-3.9	-2.6	
1,2	W1/W2, Expt.	24	Mean absolute	1.1	1.3	1.3	2.5	4.1	4.1	3.0	
1,2	W1/W2, Expt.	24	RMS	1.5	1.6	1.5	2.9	4.3	4.6	3.5	
1,2	W1/W2, Expt.	24	Max(+)	1.5	2.0	1.7	0.9	-1.7	0.8	1.8	
1,2	W1/W2, Expt.	24	Max(-)	-3.7	-3.0	-3.2	-5.0	-6.9	-7.0	-6.4	
4	W1, Expt.	10(8)	Mean	1.6(1.7)	3.1(2.8)	2.1(1.0)	3.3(1.8)	1.2(0.7)	-1.1(-1.3)	0.7(-0.2)	
4	W1, Expt.	10(8)	Mean absolute	2.8(2.1)	3.3(2.8)	2.8(1.8)	3.8(2.4)	3.2(2.1)	2.1(1.3)	2.3(1.8)	
4	W1, Expt.	10(8)	RMS	3.4(2.5)	4.3(3.2)	3.6(2.2)	5.1(3.2)	4.3(2.6)	2.9(1.6)	3.2(2.1)	
4	W1, Expt.	10(8)	Max(+)	6.8(5.1)	9.9(6.1)	6.9(4.5)	10.2(6.1)	10.6(5.3)	5.1(0.9)	8.4(3.5)	
4	W1, Expt.	10(8)	Max(-)	-4.3(-0.7)	-0.9(0.4)	-2.0(-2.0)	-1.2(-1.2)	-4.5(-2.2)	-6.0(-3.0)	-3.1(-3.1)	
3	CBS-APNO	22	Mean	0.0	0.4	0.5	-0.8	-4.1	-4.0	-2.6	2.1
3	CBS-APNO	22	Mean absolute	1.3	1.7	1.5	1.8	4.3	4.2	2.9	2.2
3	CBS-APNO	22	RMS	1.7	2.2	2.0	2.3	4.9	4.9	3.5	2.8
3	CBS-APNO	22	Max(+)	5.0	5.4	5.5	4.8	2.1	1.5	1.6	8.7
3	CBS-APNO	22	Max(-)	-2.8	-2.8	-2.9	-4.6	-9.2	-8.5	-6.7	-1.1
3	exp	32(31)	Mean	0.7	0.9	1.3	-0.8	-3.3	-3.3	-1.5	(2.9)
3	exp	32(31)	Mean absolute	1.7	1.7	1.4	1.8	3.7	3.8	3.0	(3.3)
3	exp	32(31)	RMS	2.2	2.4	1.9	2.3	4.6	4.6	3.5	(4.2)
3	exp	32(31)	Max(+)	5.6	5.9	5.7	3.1	2.2	2.6	3.8	(13.7)
3	exp	32(31)	Max(-)	-2.4	-2.5	-0.8	-2.5	-11.6	-7.9	-5.8	(-3.3)

scribed in Sec. II. We will refrain from the use of small basis sets in order to calculate transition states, in order not to blur our comparison with additional error sources such as BSSE and basis set incompleteness effects on reference geometries. During preoptimizations, we in fact found that in some difficult cases, we were unable to locate a transition state with a basis set like 6-31+G\*. Overall, the functionals developed for transition states show a strong performance throughout for the barriers. The B97-1 and B3LYP functionals yield very inconsistent results: While some reaction barriers are actually overestimated, many transition states cannot be found at all, lie below the reactants in energy (albeit above the entry channel long distance complex: examples were previously reported for  $S_N2$  reactions<sup>9,60</sup>), or are underestimated by up to 10 kcal/mol (e.g., for the transition state of the  $\text{CH}_3\text{F} + \text{H} \rightarrow \text{CH}_3 + \text{HF}$  reaction, # 63). For most reactions, B97-1 does even worse than B3LYP, usually underestimating barriers by an additional kcal/mol. It is somewhat peculiar that the forward reactions of the type  $\text{AH} + \text{H} \rightarrow \text{A} + \text{H}_2$  show a lower error for B97-1 (reactions 9–15, 36, 38, 39, 53, 63–65, and 70) than for B3LYP, with the opposite effect seen for the reverse reactions of this type (reactions 6, 7, 19, 20, and 49). B97-2 usually predicts somewhat higher barriers than B97-1.

We will now turn to the summary error statistics in Table VII. Compared to Table III—where we calculated single-point energies at the QCISD geometries—the rms errors of all functionals are further reduced. The BMK functional yields the lowest mean absolute error of 1.1 kcal/mol, showing a similar performance to B97-K and mPW1K. KMLYP yields results between the functionals which have 20% (B3LYP, B97-1) exact exchange and the ones having around

42% (BMK, B97-K, and mPW1K). While B97-2 represents an improvement over B97-1 (as noted in Ref. 90), performance for barrier heights is still clearly inferior to BMK, as well as to B97-K and mPW1K. (B97-2 and KMLYP are somewhat more closely matched.)

For the fourth set of Houk and co-workers in Table VII, we reported error statistics to either ten (25–34) or eight (25–32) reactions because of the discrepancies of the various computed values among each other and with experiment for reactions 33–35, particularly the last one. For this set, B97-1 is the only functional that underestimates the transition barriers on average and shows the lowest rms error. The rms errors of BMK and mPW1K are worse by about 0.7 kcal/mol, followed by B3LYP, B97-K, and KMLYP.

Finally, the results obtained for our training set (reactions 1–24 in Table S-1) are further validated by comparing to Kang and Musgrave's experimental numbers and their CBS-APNO calculations. Here, KMLYP yields errors comparable to the other functionals developed for transition states, probably because they used this set for determining their functional. Again, B3LYP and B97-1 show poor performance, B97-2 somewhat better. As Kang and Musgrave have already reported, G2 also yields very large errors, overestimating the experimental numbers by an average of 3 kcal/mol. For transition states, G2 seems to be less accurate than the functionals tested. This should not surprise the reader, considering the heavy reliance on low-order perturbation theory—which often has problems with transition states because of its hypersensitivity to nondynamical correlation effects—in the G2 method.

Summarizing this section, without the two presently proposed functionals one is in a dilemma about whether to com-

promise on the accuracy of equilibrium energetics (with transition state biased functionals like mPW1K and KMLYP, compare Tables III, IV, and VI with Tables VII and S-1) or on that of barrier heights (with traditional general-purpose functionals). B97-K and, in particular, BMK allow users to “have their cake and eat it too.” In fact, overall performance of BMK for all properties considered here is such that it can legitimately be considered a general-purpose functional, albeit with its applicability extended to transition states.

## V. CONCLUSIONS

Prior to this work, all exchange-correlation functionals that consistently perform reliably for transition states and barrier heights (such as BH&HLYP, mPW1K, and KMLYP) achieve this feat at the expense of seriously degraded performance for all other properties. We have developed two new exchange-correlation functionals suitable for transition states, the hybrid GGA functional B97-K (Becke-97 for kinetics) and the hybrid meta-GGA functional BMK (Boese-Martin for kinetics). These functionals, especially BMK, were parametrized against very large and diverse training sets. Both functionals achieve performance similar to mPW1K for transition states. However, B97-K and especially BMK perform much more reliably for more general properties than those earlier specialized functionals. Overall performance of B97-K is intermediate between mPW1K and the very reliable B97-1 functional (except for perhaps fortuitously excellent performance for hydrogen bonds); the BMK functional actually outperforms B3LYP for most properties and is competitive with the best currently available functionals for equilibrium energetics. Its performance for geometries and vibrational frequencies is somewhat less good than B3LYP but markedly superior to all available specialized functionals for transition states. Unlike these latter, BMK can actually be considered a reliable general-purpose functional whose capabilities have been expanded to cover transition states.

To computational chemists engaged in mechanistic studies, BMK offers a single functional capable of describing all aspects of the potential surface (energetics, kinetics, structures, ...). Initial experiments for electrical properties (to be reported on in a future paper) yield promising results as well, in part because self-interaction error issues are less acute for functionals with high percentages of Hartree-Fock exchange.

The surprisingly good performance of BMK appears to hinge on the combination of a high percentage of Hartree-Fock exchange with terms dependent on the kinetic energy density. The latter appears to afford a “back correction” for excessive Hartree-Fock exchange in systems where it is undesirable, and in effect to simulate variable exact exchange to some extent. Some evidence exists that the same properties of BMK make it more suitable for describing transition metal complexes than other hybrid functionals. These observations should shed some light on the problem of developing both more accurate and more widely applicable functionals than currently available.

In sum, we believe we have added a very useful tool to the computational chemist’s toolbox.

*Note added in revision.* A referee drew our attention to a recent paper by Zhao *et al.*<sup>91</sup> in which a successor to mPW1K, denoted BBIK (Becke-Becke 1-parameter for kinetics) was proposed. This functional combines the Becke 1988 GGA exchange functional<sup>3</sup> with Hartree-Fock exchange and Becke’s 1995 meta-GGA correlation functional.<sup>92</sup> The percentage of Hartree-Fock exchange is empirically adjusted to minimize the rms error over a small dataset of nine barrier heights, the optimum value turning out to be 42% like in the present BMK functional. Clearly, this functional was not as broadly and comprehensively parametrized as BMK or even B97-K. Furthermore, Becke himself<sup>13</sup> states: “The functional of Part IV (i.e., Ref. 92) is problematic in very weakly bound systems... and is therefore not recommended. This will be corrected in future publications.” In summary, we have reason to believe that the present BMK functional will be considerably more reliable and widely applicable than the one proposed in Ref. 91.

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