

# Long-range corrected double-hybrid density functionals

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We extend the range of applicability of our previous long-range corrected (LC) hybrid functional,  $\omega$ B97X [J.-D. Chai and M. Head-Gordon, *J. Chem. Phys.* **128**, 084106 (2008)], with a nonlocal description of electron correlation, inspired by second-order Møller–Plesset (many-body) perturbation theory. This LC “double-hybrid” density functional, denoted as  $\omega$ B97X-2, is fully optimized both at the complete basis set limit (using 2-point extrapolation from calculations using triple and quadruple zeta basis sets), and also separately using the somewhat less expensive 6-311++G(3df,3pd) basis. On independent test calculations (as well as training set results),  $\omega$ B97X-2 yields high accuracy for thermochemistry, kinetics, and noncovalent interactions. In addition, owing to its high fraction of exact Hartree–Fock exchange,  $\omega$ B97X-2 shows significant improvement for the systems where self-interaction errors are severe, such as symmetric homonuclear radical cations. © 2009 American Institute of Physics. [doi:10.1063/1.3244209]

## I. INTRODUCTION

Over the past two decades, Kohn–Sham density functional theory (KS-DFT)<sup>1,2</sup> has become the most popular electronic structure method for midsize and larger molecular systems due to its satisfactory accuracy and reasonable computational costs.<sup>3–5</sup> Although the essential ingredient of KS-DFT, the exchange–correlation density functional  $E_{xc}$ , has not been exactly known, functionals based on semilocal generalized gradient approximations have performed well in many solid-state applications. Aiming to incorporate some of the nonlocal effects missing in semilocal approximations, hybrid DFT methods, first proposed by Becke,<sup>6</sup> have further reduced the remaining errors of semilocal density functionals, which has further expanded the usefulness of DFT for practical calculations.

In common hybrid functionals, a small fraction,  $c_x$ , of the exact Hartree–Fock (HF) exchange is added to a semilocal density functional. However, in certain situations, a large fraction (even 100%) of HF exchange is needed, and such global hybrid functionals can fail qualitatively. These situations mostly occur in the asymptotic regions of molecular systems.<sup>7–9</sup> To remedy this, the development of long-range corrected (LC) hybrid functional methods<sup>10–18</sup> has recently become an active research direction to obtain improved models for  $E_{xc}$ . In the LC approach, exact HF exchange is employed for the long-range (LR) part of the interelectron repulsion operator, and an approximated exchange density functional is employed for the complementary short-range (SR) part, while the treatment for correlation remains the same (at least in functional form) as for semilocal and com-

mon hybrid functionals. Due to the inclusion of 100% LR exact exchange, this approach has considerably reduced some qualitative failures of semilocal and global hybrid functional methods.

Two issues are important to make an effective LC-DFT.<sup>12</sup> One is the development of accurate SR exchange density functionals, and the other is to find a suitable separator for the SR/LR decomposition. In the first LC scheme, an *ansatz* for the conversion of any  $E_x$  to  $E_x^{\text{SR}}$ , was proposed by Iikura *et al.*,<sup>13</sup> and has become widely used. However, the resulting LC hybrid generalized gradient approximation (GGA) functionals and variants do not outperform global hybrid GGA functionals for thermochemistry. In 2006, a different LC scheme, was proposed by Vydrov *et al.*,<sup>14</sup> based on integrating the PBE model of the exchange hole. Their LC- $\omega$ PBE functional shows improved performance for thermochemistry and barrier heights (BH), and is comparable to global hybrid GGA functionals such as B3LYP.<sup>6,19</sup> However, further improvements to this approach depend on more accurate modeling of the exchange hole, which is challenging.

As an alternative path to more accurate LC functionals, we have recently proposed a simple *ansatz* to extend any  $E_x$  to  $E_x^{\text{SR}}$ , for a SR operator that still retains considerable spatial extent.<sup>10</sup> First, the SR local spin density exchange energy density is augmented by a flexible basis functional (we employ Becke’s 1997<sup>20</sup> form) which is to be fully reoptimized to be appropriate for SR exchange (as is the corresponding correlation functional). This yields the LC hybrid  $\omega$ B97 functional. Second, recognizing that relatively small optimal  $\omega$  values mean that SR exchange still has finite extent, we also include an adjustable fraction of exact SR exchange to define the  $\omega$ B97X functional.  $\omega$ B97 and  $\omega$ B97X have shown to be accurate across a diverse set of test data, containing thermochemistry, kinetics, and noncovalent interactions.<sup>10</sup>

We have also considered the problem of optimal partitioning, and identified a conserved property (the fraction of

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TABLE I. Basis sets used for  $\omega$ B97X-2(TQZ) on the training set. cc-pV(TQ)Z denotes the TQ extrapolation to basis set limit used for PT2 correlation.

System	Basis set
G3/99 (223)	cc-pV(TQ)Z
IP (40)	cc-pV(TQ)Z
EA (25)	aug-cc-pV(TQ)Z
PA (8)	cc-pV(TQ)Z
NHTBH (38)	aug-cc-pV(TQ)Z
HTBH (38)	aug-cc-pV(TQ)Z
S22 (22)	cc-pV(TQ)Z
Atoms (10)	aug-cc-pCV(TQ)Z

exact exchange retained at midrange—approximately 0.4) of the optimal HF operators for the  $\omega$ B97X functional optimized at each value of  $\omega$ .<sup>12</sup> We have argued that this is due to the appropriateness of the underlying GGA when mixed with HF according to the distance criterion. Further support for this argument is presented elsewhere.<sup>18</sup> Similar conclusions have also been made by others with different arguments.<sup>21</sup>

However, other GGA problems associated with the lack of nonlocality of the correlation hole, such as the lack of dispersion interactions (van der Waals forces are missing), are not resolved by the LC hybrid scheme, as the correlation functionals in typical LC hybrids are treated only semilocally, which cannot capture LR correlation effects.<sup>22,23</sup> In our previous work, we followed the DFT-D scheme<sup>24</sup> to extend our  $\omega$ B97X with damped atom-atom dispersion corrections, denoted as  $\omega$ B97X-D.<sup>11</sup>  $\omega$ B97X-D allows us to obtain dispersive effects with essentially zero additional computational cost relative to  $\omega$ B97X. However, due to the smaller optimal value of  $\omega$  in  $\omega$ B97X-D, ( $\omega=0.2$  Bohr<sup>-1</sup>) the self-interaction error (SIE) of  $\omega$ B97X-D is larger than that of  $\omega$ B97X ( $\omega=0.3$  Bohr<sup>-1</sup>) and  $\omega$ B97 ( $\omega=0.4$  Bohr<sup>-1</sup>). In addition, the use of “-D” corrections introduces a large number of fixed empirical parameters into the functional (though only a

TABLE II. Optimized parameters for the  $\omega$ B97X-2(TQZ) and for the  $\omega$ B97X-2(LP). Here, the same-spin PT2 coefficient  $c_{ss}$ , and the opposite-spin PT2 coefficient  $c_{os}$ , are defined in Eq. (1), and others are defined in Eq. (28) of Ref. 10.

	$\omega$ B97X-2(TQZ)	$\omega$ B97X-2(LP)
$\omega$	0.3 Bohr <sup>-1</sup>	0.3 Bohr <sup>-1</sup>
$c_{x\sigma,0}$	$3.15503 \times 10^{-1}$	$2.51767 \times 10^{-1}$
$c_{c\sigma\sigma,0}$	$9.08460 \times 10^{-1}$	1.15698
$c_{ca\beta,0}$	$5.18198 \times 10^{-1}$	$5.53261 \times 10^{-1}$
$c_{x\sigma,1}$	1.04772	1.57375
$c_{c\sigma\sigma,1}$	-2.80936	-3.31669
$c_{ca\beta,1}$	$-5.85956 \times 10^{-1}$	-1.16626
$c_{x\sigma,2}$	-2.33506	-5.26624
$c_{c\sigma\sigma,2}$	6.02676	6.27265
$c_{ca\beta,2}$	4.27080	6.84409
$c_{x\sigma,3}$	3.19909	6.74313
$c_{c\sigma\sigma,3}$	-4.56981	-4.51464
$c_{ca\beta,3}$	-6.48897	-8.90640
$c_x$	$6.36158 \times 10^{-1}$	$6.78792 \times 10^{-1}$
$c_{ss}$	$5.29319 \times 10^{-1}$	$5.81569 \times 10^{-1}$
$c_{os}$	$4.47105 \times 10^{-1}$	$4.77992 \times 10^{-1}$

damping parameter was explicitly optimized in the development of  $\omega$ B97X-D), which is undesirable for first-principles methods.

There are other methods that are under active development for treating nonlocal correlations. The van der Waals density functional approach pioneered by Rydberg *et al.*<sup>25</sup> is one promising direction, though numerical integrations are required, and the level of accuracy is still in the process of being brought to a satisfactory level.<sup>26</sup> The real-space post-HF models of Becke and Johnson<sup>27</sup> are a second direction that shows great promise. A third direction attracting considerable interest is the addition of nonlocal correlation based on the random phase approximation.<sup>28</sup>

To date, however, perhaps the most successful approach in practice to including nonlocal correlation effects is provided by the double-hybrid (DH) methods,<sup>29–33</sup> which mix both the HF exchange and a nonlocal orbital correlation energy from the second-order perturbation energy expression in wave function theory. There are typically only 1 or 2 empirical parameters for scaling the components of nonlocal correlation. Moreover, due to the presence of nonlocal correlation in DH functionals, the corresponding fractions of HF exchange is noticeably higher than for conventional hybrid functionals, as HF exchange is compatible with nonlocal correlation. The sharp increase in HF exchange in DH functionals thus greatly reduces the SIE relative to typical hybrid functionals.

In this work, we demonstrate the usefulness of a combined LC and DH scheme. The performance of this LCDH functional is compared with other hybrid, LC hybrid, and DH functionals.

## II. THE LCDH SCHEME

Similar to the existing DH scheme,<sup>29–33</sup> LC-DFT can be extended to include nonlocal orbital correlation energy from second-order Møller–Plesset perturbation (MP2) theory,<sup>34</sup> that includes a same-spin (ss) component  $E_c^{ss}$  and an opposite-spin (os) component  $E_c^{os}$ . The two parameters,  $c_{ss}$  and  $c_{os}$ , are introduced to adjust the amounts of  $E_c^{ss}$  and  $E_c^{os}$  in LCDH.

$$E_{\text{total}} = E_{\text{LC-DFT}} + c_{ss}E_c^{ss} + c_{os}E_c^{os}. \quad (1)$$

The first LCDH functional, mixing PT2 correlation with a LC hybrid functional, was proposed by Ángyán *et al.*<sup>16</sup> In their LCDH functional, the SR  $xc$  energy was treated by density functional and the LR part was treated by MP2 theory. The relevant work in this direction has had promising results for nonbonded complexes.<sup>17</sup> By contrast, our LCDH in Eq. (1) is a simplified version. The exchange part is treated by the range-separated hybrids, while the correlation part is treated by global hybrids. Our simplified LCDH functional thus avoids the need to model the SR correlation,

TABLE III. Statistical errors (in kcal/mol) of the training set. The B97-2(LP)\* functional is defined in the text. The results for  $\omega$ B97X-2(TQZ) are obtained with the basis sets and extrapolation scheme described in Table I and in the text. The results for the  $\omega$ B97X-D are taken from Ref. 11, and the results for the  $\omega$ B97X and  $\omega$ B97 are taken from Ref. 10.

System	Error	$\omega$ B97X-2(TQZ)	$\omega$ B97X-2(LP)	B97-2(LP)*	$\omega$ B97X-D	$\omega$ B97X	$\omega$ B97	B2PLYP-D*	B2PLYP*	SCS-MP2*
G3/99 (223)	MSE	0.02	-0.10	-0.05	-0.10	-0.09	-0.20	-0.56	0.10	0.36
	MAE	1.43	1.52	1.46	1.93	2.09	2.56	2.44	3.34	4.19
	rms	2.28	2.07	2.02	2.75	2.86	3.51	3.37	4.32	5.55
IP (40)	MSE	-0.66	-0.14	0.19	0.19	-0.15	-0.48	-0.98	-0.91	-2.21
	MAE	1.57	1.73	1.71	2.74	2.69	2.65	2.26	2.21	3.82
	rms	2.16	2.37	2.38	3.62	3.59	3.58	2.69	2.61	5.47
EA (25)	MSE	0.06	-0.29	0.03	0.10	-0.43	-1.45	-1.43	-1.11	-2.85
	MAE	1.42	1.56	1.47	1.92	2.05	2.67	2.08	1.75	4.75
	rms	1.99	2.23	2.42	2.40	2.59	3.10	2.37	2.09	6.40
PA (8)	MSE	-1.06	-0.80	-0.71	1.49	0.60	0.68	-0.89	-1.16	0.57
	MAE	1.19	1.09	0.97	1.54	1.22	1.45	1.06	1.19	1.22
	rms	1.39	1.32	1.27	2.11	1.72	2.17	1.31	1.43	1.32
NHTBH (38)	MSE	0.48	0.54	0.21	-0.42	0.56	1.32	-2.38	-2.34	6.47
	MAE	1.29	1.67	1.88	1.51	1.75	2.31	2.52	2.48	6.52
	rms	1.99	2.53	2.85	2.00	2.08	2.82	3.04	3.07	9.39
HTBH (38)	MSE	-0.04	-0.13	-0.33	-2.52	-1.51	-0.34	-2.60	-2.35	7.32
	MAE	0.65	0.74	0.82	2.64	2.24	2.24	2.62	2.43	7.32
	rms	0.83	0.94	1.01	3.04	2.58	2.62	2.78	2.63	15.10
S22 (22)	MSE	-0.10	-0.08	-0.07	-0.08	0.53	0.16	-0.08	2.23	1.13
	MAE	0.26	0.24	0.23	0.22	0.87	0.60	0.16	2.23	1.13
	rms	0.29	0.28	0.28	0.27	1.30	0.80	0.22	2.81	1.51
Atoms (10)	MSE	-0.20	-0.08	0.57	0.47	0.17	-0.79	1.89	2.06	37.74
	MAE	2.14	2.49	2.84	2.77	1.63	3.53	3.18	3.46	37.74
	rms	2.67	2.94	3.30	3.25	1.91	4.26	3.85	4.17	45.26
All (404)	MSE	-0.04	-0.07	-0.02	-0.27	-0.14	-0.15	-0.94	-0.40	2.11
	MAE	1.31	1.43	1.42	1.96	2.04	2.42	2.29	2.87	5.31
	rms	2.06	2.04	2.08	2.73	2.73	3.26	3.06	3.70	10.15

which is not widely available,<sup>35</sup> compared to the availability of SR exchange. We adopt our  $\omega$ B97X [see Eq. (28) of Ref. 10] for the LC-DFT part and denote this new LCDH functional as  $\omega$ B97X-2, where the “-2” refers to the post-KS treatment for the nonlocal (orbital) correlation energy taken from second-order perturbation theory.

To achieve an optimized functional for well-balanced performance across typical chemical applications, we use the same diverse training set described in Ref. 10, which contains 404 accurate experimental and accurate theoretical results, including the 10 atomic energies from the H atom to the Ne atom,<sup>36</sup> the atomization energies (AEs) of the G3/99 set<sup>37-39</sup> (223 molecules), the ionization potentials (IPs) of the G2-1 set<sup>40</sup> [40 molecules, excluding SH<sub>2</sub> (<sup>2</sup>A<sub>1</sub>) and N<sub>2</sub> (<sup>2</sup>Π) cations due to the known convergence problems for semilocal density functionals<sup>38</sup>], the electron affinities (EAs) of the G2-1 set (25 molecules), the proton affinities (PAs) of the G2-1 set (8 molecules), the 76 BHs of the NHTBH38/04 and HTBH38/04 sets,<sup>41,42</sup> and the 22 noncovalent interactions of the S22 set.<sup>43</sup>

To adequately converge the PT2 correlation energy toward the complete basis set limit,  $E_\infty$ , we adopt the standard two-point extrapolation<sup>44</sup> for cc-pVXZ (or aug-cc-pVXZ or aug-cc-pCVXZ) to the expression

$$E_\infty = E(X) + cX^{-3}, \quad (2)$$

where  $c$  is a constant, and  $X$  is 3 for  $T$  and 4 for  $Q$ .

We denote our LCDH functional parameterized with this  $TQ$  extrapolation as  $\omega$ B97X-2(TQZ). For certain types of calculations, such as EAs and BHs, the use of diffuse basis sets is found to be important, and we adopt the corresponding “aug” (augmented) basis sets. For atomic energies, we further include the “core” effects with core-valence (CV) basis set, aug-cc-pCVXZ. For  $XC$  grids, we use the extra fine grid, EML(99,590), consisting of 99 Euler–Maclaurin radial grid points<sup>45</sup> and 590 Lebedev angular grid points<sup>46</sup> for atomic energies, and EML(75,302) for others. In Table I, we summarize the basis sets used to parameterize  $\omega$ B97X-2(TQZ). For some calculations, the resolution-of-identity (RI) approximation<sup>47</sup> is used for the PT2 calculations with suitable auxiliary basis sets.

For practical calculations on large systems, the use of the large cc-pVQZ or aug-cc-pVQZ basis sets becomes computationally prohibitive. To partially circumvent this limitation, we have also parameterized the same LCDH functional with the Large Pople (LP) type basis set, 6-311++G(3df,3pd), which we denote as  $\omega$ B97X-2(LP). We use the LP basis set and the SG-1 grid<sup>48</sup> together with the RI approximation for PT2 calculations, where very large auxiliary basis sets (i.e., cc-pVQZ or aug-cc-pVQZ) are used.

To prevent double-counting of energy contributions from the LC-DF and from the PT2 correlation, all the parameters in  $\omega$ B97X-2, are determined self-consistently by the least-squares fitting procedure described in Ref. 10. For the non-

TABLE IV. Statistical errors (in kcal/mol) of the training set.

System	Error	B2PLYP-D	B2PLYP	SCS-MP2	MP2
G3/99 (223)	MSE	-1.48	-3.21	-1.58	5.42
	MAE	2.63	3.96	4.03	9.16
	rms	3.60	5.26	5.34	12.44
IP (40)	MSE	-1.04	-1.04	-2.40	-1.69
	MAE	2.29	2.29	3.98	3.59
	rms	2.73	2.72	5.58	5.00
EA (25)	MSE	-1.51	-1.50	-3.14	-1.67
	MAE	2.17	2.17	5.03	3.95
	rms	2.45	2.44	6.57	5.67
PA (8)	MSE	-0.90	-1.08	0.75	-0.93
	MAE	1.08	1.17	1.32	0.96
	rms	1.33	1.39	1.46	1.20
NHTBH (38)	MSE	-2.29	-2.00	6.61	5.37
	MAE	2.44	2.19	6.65	5.48
	rms	2.94	2.68	9.49	8.45
HTBH (38)	MSE	-2.49	-2.01	7.55	5.84
	MAE	2.52	2.11	7.55	6.54
	rms	2.69	2.32	15.20	14.68
S22 (22)	MSE	0.08	2.30	1.30	-0.17
	MAE	0.21	2.30	1.30	0.75
	rms	0.29	2.93	1.68	1.04
Atoms (10)	MSE	8.00	8.00	38.00	39.15
	MAE	8.00	8.00	38.00	39.15
	rms	9.20	9.20	45.75	45.79
All (404)	MSE	-1.28	-2.04	1.06	4.72
	MAE	2.51	3.29	5.30	7.81
	rms	3.45	4.49	10.19	13.00

linear parameter optimization, we focus on a discrete set of possible  $\omega$  values (0.0, 0.1, 0.2, 0.3, 0.4, and 0.5 Bohr<sup>-1</sup>). The functional expansions employed in  $\omega$ B97X-2 are truncated at  $m=3$ , and the S22 data is weighted ten times more than others.

Although the  $\omega$  value of  $\omega$ B97X-2 was found to be optimal at 0.2 Bohr<sup>-1</sup>, the rms errors at each  $\omega$  are, however, very insensitive. We thus fix the final  $\omega$  value to be 0.3 Bohr<sup>-1</sup>, based on comparably good performance in the training set as well improved performance in systems with severe SIE issues. The optimized parameters of the  $\omega$ B97X-2 functional parametrized with  $TQ$  extrapolation to the basis set limit ( $TQZ$ ) and with the LP basis sets are given in Table II.

The limiting case where  $\omega=0$  for  $\omega$ B97X-2 is also very interesting, as it reduces to a reoptimized B97 functional<sup>20</sup> augmented with the scaled PT2 correlation. For comparisons within the training set, we denote this reoptimized functional (parameterized with the LP basis set) as B97-2(LP)\*. We also reoptimize B2PLYP-D, B2PLYP, and SCS-MP2 on the same training set and with the same enhanced weight for the S22 set. We denote these reoptimized functionals as B2PLYP-D\*, B2PLYP\*, and SCS-MP2\*. The overall performance of all these functionals parameterized on the same training set [including our previous LC hybrid functionals,  $\omega$ B97,<sup>10</sup>  $\omega$ B97X,<sup>10</sup> and  $\omega$ B97X-D (Ref. 11)] is shown in Table III

The overall performance of B2PLYP,<sup>29</sup> B2PLYP-D,<sup>30</sup> SCS-MP2,<sup>49</sup> and MP2,<sup>34</sup> although not optimized in the training set, is shown in Table IV for comparison with their re-

optimized versions. Note that the SCS-MP2 and MP2 methods are truly self-interaction-free methods with similar cost as all the DH and LCDH functionals.

### III. RESULTS AND DISCUSSION

#### A. The training set

All calculations are performed with a development version of Q-Chem 3.0.<sup>50</sup> Spin-restricted theory is used for singlet states and spin-unrestricted theory for others. For the binding energies of the weakly bound systems, the counterpoise correction<sup>51</sup> is employed to reduce basis set superposition errors (BSSE).

The error for each entry is defined as error = theoretical value - reference value. The notation used for characterizing statistical errors is as follows: mean signed errors (MSEs), mean absolute errors (MAEs), rms errors, maximum negative errors [max(-)], and maximum positive errors [max(+)].

As can be seen in Table III, our new LCDH functionals,  $\omega$ B97X-2( $TQZ$ ) and  $\omega$ B97X-2(LP), achieve very high accuracy. Many comparisons are possible, and we summarize a few of the most important conclusions in the following paragraphs.

Let us compare the new LCDH functionals to other DH functionals trained on the same data. It is evident that B97-2(LP)\* performs almost identically to  $\omega$ B97X-2(LP), since, as already discussed, the rms errors are very insensi-



TABLE V. Nonhydrogen transfer BHs (in kcal/mol) of the NHTBH38/04 set (Ref. 42). The results for the  $\omega$ B97X-D are taken from Ref. 11, and the results for the  $\omega$ B97X and  $\omega$ B97 are taken from Ref. 10.

Reactions	$\Delta E_{\text{ref}}$	$\omega$ B97X-2(LP)	$\omega$ B97X-D	$\omega$ B97X	$\omega$ B97	B2PLYP-D	B2PLYP	SCS-MP2	MP2	
H+N <sub>2</sub> O→OH+N <sub>2</sub>	$V^f$	18.14	21.14	17.45	19.22	20.67	16.50	16.67	36.81	36.05
	$V^r$	83.22	84.13	77.73	80.57	81.93	76.42	76.62	97.54	88.32
H+FH→HF+H	$V^f$	42.18	42.07	40.54	43.10	44.78	36.53	36.66	48.61	46.57
	$V^r$	42.18	42.07	40.54	43.10	44.78	36.53	36.66	48.61	46.57
H+ClH→HCl+H	$V^f$	18.00	19.17	18.24	20.73	23.17	15.67	15.70	23.50	22.64
	$V^r$	18.00	19.17	18.24	20.73	23.17	15.67	15.70	23.50	22.64
H+FCH <sub>3</sub> →HF+CH <sub>3</sub>	$V^f$	30.38	30.61	30.10	32.14	33.46	26.18	26.55	38.00	36.14
	$V^r$	57.02	56.38	54.56	55.41	55.83	52.27	52.70	62.85	60.23
H+F <sub>2</sub> →HF+F	$V^f$	2.27	9.71	-0.64	0.86	1.96	0.81	0.86	29.13	28.32
	$V^r$	106.18	115.83	103.97	104.27	103.66	106.35	106.41	135.50	133.73
CH <sub>3</sub> +FCl→CH <sub>3</sub> F+Cl	$V^f$	7.43	7.31	2.84	3.93	4.62	1.85	2.53	20.79	18.72
	$V^r$	60.17	61.74	56.60	58.52	59.96	56.16	56.77	77.76	75.15
F <sup>-</sup> +CH <sub>3</sub> F→FCH <sub>3</sub> +F <sup>-</sup>	$V^f$	-0.34	-3.52	-1.36	-2.27	-2.60	-3.69	-3.20	1.40	0.37
	$V^r$	-0.34	-3.52	-1.36	-2.27	-2.60	-3.69	-3.20	1.40	0.37
F <sup>-</sup> ⋯CH <sub>3</sub> F→FCH <sub>3</sub> ⋯F <sup>-</sup>	$V^f$	13.38	12.13	12.91	13.28	13.32	11.45	11.29	15.39	14.75
	$V^r$	13.38	12.13	12.91	13.28	13.32	11.45	11.29	15.39	14.75
Cl <sup>-</sup> +CH <sub>3</sub> Cl→ClCH <sub>3</sub> +Cl <sup>-</sup>	$V^f$	3.10	2.38	3.71	4.71	6.21	0.22	1.01	6.40	5.50
	$V^r$	3.10	2.38	3.71	4.71	6.21	0.22	1.01	6.40	5.50
Cl <sup>-</sup> ⋯CH <sub>3</sub> Cl→ClCH <sub>3</sub> ⋯Cl <sup>-</sup>	$V^f$	13.61	13.90	14.37	16.09	17.74	11.33	11.41	16.89	16.54
	$V^r$	13.61	13.90	14.37	16.09	17.74	11.33	11.41	16.89	16.54
F <sup>-</sup> +CH <sub>3</sub> Cl→FCH <sub>3</sub> +Cl <sup>-</sup>	$V^f$	-12.54	-13.92	-13.47	-13.11	-11.72	-15.67	-15.07	-9.84	-10.28
	$V^r$	20.11	18.08	21.36	20.83	20.15	17.98	18.62	22.51	20.70
F <sup>-</sup> ⋯CH <sub>3</sub> Cl→FCH <sub>3</sub> ⋯Cl <sup>-</sup>	$V^f$	2.89	3.39	3.16	4.23	5.39	1.78	1.72	5.63	5.66
	$V^r$	29.62	28.62	30.70	31.19	30.95	27.75	27.73	32.01	30.64
OH <sup>-</sup> +CH <sub>3</sub> F→HOCH <sub>3</sub> +F <sup>-</sup>	$V^f$	-2.78	-5.28	-3.32	-3.70	-4.05	-5.88	-5.06	-0.35	-1.71
	$V^r$	17.33	14.90	18.05	17.64	17.86	14.02	14.61	18.98	17.96
OH <sup>-</sup> ⋯CH <sub>3</sub> F→HOCH <sub>3</sub> ⋯F <sup>-</sup>	$V^f$	10.96	10.09	10.50	11.47	11.52	8.74	8.99	13.44	12.58
	$V^r$	47.20	47.05	49.18	49.33	49.13	45.91	46.16	49.71	50.20
H+N <sub>2</sub> →HN <sub>2</sub>	$V^f$	14.69	16.56	12.32	13.99	15.47	12.26	12.33	28.17	27.64
	$V^r$	10.72	11.56	13.42	14.32	15.06	10.65	10.71	9.86	8.65
H+CO→HCO	$V^f$	3.17	3.52	3.37	4.55	5.65	1.68	1.82	6.37	5.93
	$V^r$	22.68	24.33	26.16	26.72	27.07	24.00	24.09	22.87	22.70
H+C <sub>2</sub> H <sub>4</sub> →CH <sub>3</sub> CH <sub>2</sub>	$V^f$	1.72	3.44	2.99	4.07	4.94	1.31	1.81	10.00	9.35
	$V^r$	41.75	45.42	45.49	47.07	48.49	42.30	42.52	48.05	46.58
CH <sub>3</sub> +C <sub>2</sub> H <sub>4</sub> →CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub>	$V^f$	6.85	7.61	4.57	5.04	4.81	5.66	7.15	14.99	12.87
	$V^r$	32.97	35.86	33.59	35.21	36.59	32.02	32.36	41.45	41.52
HNC→HNC	$V^f$	48.16	49.63	46.43	46.29	45.89	48.76	48.68	52.29	52.21
	$V^r$	33.11	33.59	33.22	33.12	32.80	33.38	33.32	35.41	34.80
MSE			0.54	-0.42	0.56	1.32	-2.29	-2.00	6.61	5.37
MAE			1.67	1.51	1.75	2.31	2.44	2.19	6.65	5.48
rms			2.53	2.00	2.08	2.82	2.94	2.68	9.49	8.45
Max (-)			-3.18	-5.49	-3.50	-2.81	-6.80	-6.60	-0.86	-2.07
Max (+)			9.65	3.74	5.32	6.74	1.32	1.41	29.32	27.55

tive to  $\omega$ . Therefore there is little benefit to the LCDH scheme relative to a fully reoptimized DH functional on this data set. The principal benefit will be reduced SIE, as will be evaluated later. However, both  $\omega$ B97X-2(LP) and B97-2(LP)\* performed significantly better than the reoptimized B2PLYP-D\* and B2PLYP\* DH functionals. This indicates the importance of flexible GGA forms even in the DH functionals: the GGA is held fixed in the definition of B2PLYP-D\* and B2PLYP\*.

Comparison between this new LCDH functional and our previous LC hybrids,  $\omega$ B97X-D,  $\omega$ B97X, and  $\omega$ B97, shows that  $\omega$ B97X-2 consistently improves LC hybrids. This indicates the usefulness of augmenting LC hybrids with nonlocal correlation. In particular, relative to  $\omega$ B97X-D,  $\omega$ B97X-2

performs similarly for the S22 intermolecular interactions, and significantly better for thermochemical calculations.

Finally, the reoptimized SCS-MP2\*, though free from SIE, performs most poorly of all approaches shown in Table III, due to the lack of mixing with semilocal density functionals. Additionally, for reference the performance of existing methods that are not optimized on the training set, B2PLYP-D, B2PLYP, SCS-MP2, and MP2, are listed in Table IV for comparison. More detailed results for the training set are given in Tables V–VII.

Since the  $\omega$ B97X-2 contains orbital correlation through the PT2 contribution, its energy converges more slowly as the basis set is enlarged than LC hybrids. As can be seen in Table VIII,  $\omega$ B97X-2(TQZ) performs best with the TQ ex-

TABLE VI. Hydrogen transfer BHs (in kcal/mol) of the HTBH38/04 set (Refs. 41 and 42). The results for the  $\omega$ B97X-D are taken from Ref. 11, and the results for the  $\omega$ B97X and  $\omega$ B97 are taken from Ref. 10.

Reactions	$\Delta E_{\text{ref}}$	$\omega$ B97X-2(LP)	$\omega$ B97X-D	$\omega$ B97X	$\omega$ B97	B2PLYP-D	B2PLYP	SCS-MP2	MP2
H+HCl $\rightarrow$ H <sub>2</sub> +Cl	$V^f$ 5.7	5.25	4.22	5.33	6.68	2.78	2.84	9.08	10.68
	$V^r$ 8.7	6.62	4.51	5.24	6.49	5.38	5.44	10.21	7.45
OH+H <sub>2</sub> $\rightarrow$ H+H <sub>2</sub> O	$V^f$ 5.1	5.12	2.24	2.56	3.27	2.71	2.92	10.05	7.27
	$V^r$ 21.2	21.77	18.76	19.50	20.39	18.35	18.55	29.14	31.87
CH <sub>3</sub> +H <sub>2</sub> $\rightarrow$ H+CH <sub>4</sub>	$V^f$ 12.1	11.62	9.14	9.63	10.29	9.69	10.23	14.56	12.76
	$V^r$ 15.3	14.99	13.67	15.13	16.35	12.30	12.78	19.11	19.76
OH+CH <sub>4</sub> $\rightarrow$ CH <sub>3</sub> +H <sub>2</sub> O	$V^f$ 6.7	5.60	3.19	3.97	4.53	3.30	3.88	10.49	7.19
	$V^r$ 19.6	18.87	15.17	15.41	15.59	16.33	16.96	25.04	24.79
H+H <sub>2</sub> $\rightarrow$ H <sub>2</sub> +H	$V^f$ 9.6	9.86	9.22	10.74	12.38	7.03	7.12	13.49	13.24
	$V^r$ 9.6	9.86	9.22	10.74	12.38	7.03	7.12	13.49	13.24
OH+NH <sub>3</sub> $\rightarrow$ H <sub>2</sub> O+NH <sub>2</sub>	$V^f$ 3.2	3.16	0.01	1.62	2.83	-0.46	0.12	10.10	6.40
	$V^r$ 12.7	13.42	9.68	10.97	12.10	9.80	10.41	21.10	18.62
HCl+CH <sub>3</sub> $\rightarrow$ Cl+CH <sub>4</sub>	$V^f$ 1.7	0.50	-1.67	-1.07	-0.47	-0.90	-0.18	64.92	64.14
	$V^r$ 7.9	5.24	3.15	4.34	5.41	4.31	4.97	70.60	67.91
OH+C <sub>2</sub> H <sub>6</sub> $\rightarrow$ H <sub>2</sub> O+C <sub>2</sub> H <sub>5</sub>	$V^f$ 3.4	3.06	0.33	1.26	1.85	0.46	1.11	8.17	4.94
	$V^r$ 19.9	19.83	16.61	17.22	17.31	17.23	18.19	25.46	25.50
F+H <sub>2</sub> $\rightarrow$ HF+H	$V^f$ 1.8	0.95	-3.70	-3.89	-3.76	-1.79	-1.67	5.92	4.37
	$V^r$ 33.4	33.88	28.98	29.17	29.80	30.28	30.40	41.17	46.07
O+CH <sub>4</sub> $\rightarrow$ OH+CH <sub>3</sub>	$V^f$ 13.7	12.70	9.36	9.94	10.45	10.05	10.47	18.12	15.88
	$V^r$ 8.1	8.59	4.69	4.85	4.82	6.27	6.76	13.00	11.49
H+PH <sub>3</sub> $\rightarrow$ PH <sub>2</sub> +H <sub>2</sub>	$V^f$ 3.1	3.10	3.22	4.62	5.88	1.08	1.31	5.81	5.50
	$V^r$ 23.2	23.83	23.41	24.11	25.25	22.93	23.48	26.31	24.04
H+HO $\rightarrow$ H <sub>2</sub> +O	$V^f$ 10.7	11.59	8.78	9.79	10.68	8.12	8.18	17.30	17.76
	$V^r$ 13.1	12.32	8.92	9.38	10.26	9.28	9.33	17.87	15.15
H+H <sub>2</sub> S $\rightarrow$ H <sub>2</sub> +HS	$V^f$ 3.5	4.02	4.07	5.54	6.94	1.78	1.95	6.94	6.66
	$V^r$ 17.3	16.89	16.27	17.16	18.42	15.96	16.25	19.59	16.11
O+HCl $\rightarrow$ OH+Cl	$V^f$ 9.8	10.91	5.63	7.07	14.21	6.53	6.57	17.99	15.25
	$V^r$ 10.4	11.55	5.77	7.38	14.45	7.97	8.01	18.54	14.63
NH <sub>2</sub> +CH <sub>3</sub> $\rightarrow$ CH <sub>4</sub> +NH	$V^f$ 8.0	8.91	5.67	6.50	6.95	6.93	7.74	12.61	10.61
	$V^r$ 22.4	21.52	18.54	19.42	20.07	18.82	19.57	25.43	23.70
NH <sub>2</sub> +C <sub>2</sub> H <sub>5</sub> $\rightarrow$ C <sub>2</sub> H <sub>6</sub> +NH	$V^f$ 7.5	9.83	7.38	8.48	8.82	8.04	9.13	13.05	10.93
	$V^r$ 18.3	18.93	15.95	16.87	17.54	16.18	16.97	23.13	21.06
C <sub>2</sub> H <sub>6</sub> +NH <sub>2</sub> $\rightarrow$ NH <sub>3</sub> +C <sub>2</sub> H <sub>5</sub>	$V^f$ 10.4	10.89	8.81	10.16	11.01	8.83	9.83	14.57	11.19
	$V^r$ 17.4	17.41	15.42	16.77	17.21	15.35	16.62	20.85	19.54
NH <sub>2</sub> +CH <sub>4</sub> $\rightarrow$ CH <sub>3</sub> +NH <sub>3</sub>	$V^f$ 14.5	13.51	11.39	12.64	13.49	11.57	12.46	16.99	13.84
	$V^r$ 17.8	16.52	13.70	14.72	15.29	14.34	15.25	20.53	19.23
<i>s-trans</i> <i>cis</i> -C <sub>3</sub> H <sub>8</sub> $\rightarrow$ <i>s-trans</i> <i>cis</i> -C <sub>3</sub> H <sub>8</sub>	$V^f$ 38.4	37.99	39.06	41.44	42.84	37.55	38.07	39.84	33.30
	$V^r$ 38.4	37.99	39.06	41.44	42.84	37.55	38.07	39.84	33.30
MSE		-0.13	-2.52	-1.51	-0.34	-2.49	-2.01	7.55	5.84
MAE		0.74	2.64	2.24	2.24	2.52	2.11	7.55	6.54
rms		0.94	3.04	2.58	2.62	2.69	2.32	15.20	14.68
Max (-)		-2.66	-5.50	-5.69	-5.56	-3.82	-3.77	1.44	-5.10
Max (+)		2.33	0.66	3.04	4.44	0.54	1.63	63.22	62.44

trapolation procedure (*TQZ*), while it performs less satisfactorily with smaller basis sets. This data shows the importance of using  $\omega$ B97X-2 with the basis sets for which it is optimized—either the approximation to the complete basis set limit,  $\omega$ B97X-2(*TQZ*), or the alternative development for the LP basis,  $\omega$ B97X-2(LP).

## B. The test sets

To test the performance of  $\omega$ B97X-2 outside its training set, we also evaluate its performance on various test sets involving the additional 48 AEs in the G3/05 test set<sup>52</sup> (other than the 223 AEs in the G3/99 test set<sup>37-39</sup>), 30 chemical

reaction energies taken from the NHTBH38/04 and HTBH38/04 databases,<sup>41,42</sup> 29 noncovalent interactions,<sup>43,53</sup> and 4 dissociation curves of symmetric radical cations. There are a total of 111 pieces of data in the test sets. Due to the large sizes of molecules in the test sets, we have only tested the performance of  $\omega$ B97X-2(LP), which was parameterized with the LP basis set. More detailed information about the test sets as well as the basis sets, and numerical grids used is given in Ref. 10. We use either full PT2 correlation (without RI approximation), or, for efficiency, we evaluate PT2 correlation with the RI approximation and large auxiliary basis sets. There is no chemically significant difference.

The additional 48 AEs in the G3/05 test set<sup>52</sup> are com-

TABLE VII. Interaction energies (in kcal/mol) for the S22 set (Ref. 43). The counterpoise corrections are used to reduce the basis set superposition errors. Monomer deformation energies are not included. The results for the  $\omega$ B97X-D are taken from Ref. 11, and the results for the  $\omega$ B97X and  $\omega$ B97 are taken from Ref. 10.

Complex [symmetry]	$\Delta E_{\text{ref}}$	$\omega$ B97X-2(LP)	$\omega$ B97X-D	$\omega$ B97X	$\omega$ B97	B2PLYP-D	B2PLYP	SCS-MP2	MP2
Hydrogen bonded complexes									
(NH <sub>3</sub> ) <sub>2</sub> [C <sub>2h</sub> ]	-3.17	-3.35	-3.07	-3.58	-3.64	-3.32	-2.56	-2.50	-2.92
(H <sub>2</sub> O) <sub>2</sub> [C <sub>s</sub> ]	-5.02	-5.24	-4.97	-5.59	-5.64	-5.08	-4.66	-4.14	-4.61
Formic acid dimer [C <sub>2h</sub> ]	-18.61	-18.76	-19.30	-19.96	-20.13	-18.90	-17.52	-15.47	-17.16
Formamide dimer [C <sub>2h</sub> ]	-15.96	-15.80	-16.16	-16.65	-16.78	-15.95	-14.49	-13.27	-14.68
Uracil dimer [C <sub>2h</sub> ]	-20.65	-20.13	-20.44	-20.30	-20.31	-20.51	-18.67	-17.29	-19.22
2-pyridoxine·2-aminopyridine [C <sub>1</sub> ]	-16.71	-16.70	-17.06	-16.37	-16.40	-17.11	-14.93	-14.23	-16.29
Adenine·thymine WC [C <sub>1</sub> ]	-16.37	-16.11	-16.45	-15.91	-16.05	-16.48	-14.15	-13.54	-15.47
MSE		0.06	-0.14	-0.27	-0.35	-0.12	1.36	2.29	0.88
MAE		0.22	0.24	0.60	0.63	0.17	1.36	2.29	0.88
Dispersion complexes									
(CH <sub>4</sub> ) <sub>2</sub> [D <sub>3d</sub> ]	-0.53	-0.70	-0.57	-0.57	-0.44	-0.40	0.05	-0.25	-0.42
(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub> [D <sub>2d</sub> ]	-1.51	-1.76	-1.78	-1.77	-1.92	-1.45	-0.27	-0.82	-1.35
Benzene·CH <sub>4</sub> [C <sub>3</sub> ]	-1.50	-1.69	-1.68	-1.41	-1.55	-1.33	-0.13	-0.99	-1.64
Benzene dimer [C <sub>2h</sub> ]	-2.73	-3.25	-3.19	-1.57	-2.33	-2.32	0.83	-2.50	-4.58
Pyrazine dimer [C <sub>s</sub> ]	-4.42	-4.82	-4.25	-2.86	-3.68	-4.12	-0.70	-4.14	-6.38
Uracil dimer [C <sub>2</sub> ]	-10.12	-9.72	-9.79	-7.84	-8.90	-9.68	-4.72	-7.59	-10.32
Indole·benzene [C <sub>1</sub> ]	-5.22	-5.23	-5.05	-2.39	-3.58	-4.36	0.33	-4.42	-7.56
Adenine·thymine stack [C <sub>1</sub> ]	-12.23	-11.81	-11.81	-8.40	-10.26	-11.85	-4.58	-9.73	-13.86
MSE		-0.09	0.02	1.43	0.70	0.34	3.63	0.98	-0.98
MAE		0.30	0.25	1.51	0.82	0.34	3.63	0.98	1.05
Mixed complexes									
Ethene·ethine [C <sub>2v</sub> ]	-1.53	-1.72	-1.64	-1.67	-1.63	-1.54	-0.99	-1.18	-1.52
Benzene·H <sub>2</sub> O [C <sub>s</sub> ]	-3.28	-3.51	-3.50	-3.39	-3.56	-3.33	-2.05	-2.62	-3.25
Benzene·NH <sub>3</sub> [C <sub>s</sub> ]	-2.35	-2.55	-2.54	-2.31	-2.46	-2.26	-1.01	-1.80	-2.43
Benzene·HCN [C <sub>s</sub> ]	-4.46	-4.88	-4.79	-4.61	-4.89	-4.77	-3.07	-3.87	-4.78
Benzene dimer [C <sub>2v</sub> ]	-2.74	-2.99	-2.89	-2.11	-2.38	-2.63	-0.63	-2.21	-3.36
Indole·benzene T-shape [C <sub>1</sub> ]	-5.73	-5.82	-5.63	-4.44	-4.82	-5.71	-2.79	-4.86	-6.53
Phenol dimer [C <sub>1</sub> ]	-7.05	-7.18	-6.98	-6.49	-6.93	-6.95	-4.71	-5.79	-7.22
MSE		-0.22	-0.12	0.30	0.07	-0.01	1.70	0.69	-0.28
MAE		0.22	0.17	0.42	0.33	0.10	1.70	0.69	0.29
MSE		-0.08	-0.08	0.53	0.16	0.08	2.30	1.30	-0.17
MAE		0.24	0.22	0.87	0.60	0.21	2.30	1.30	0.75
rms		0.28	0.27	1.30	0.80	0.29	2.93	1.68	1.04
Max (-)		-0.52	-0.69	-1.35	-1.52	-0.40	0.36	0.23	-2.34
Max (+)		0.52	0.42	3.83	1.97	0.86	7.65	3.36	1.45

TABLE VIII. Statistical errors (in kcal/mol) of the training set. MAE (in kcal/mol) of  $\omega$ B97X-2(TQZ) on the training set, using four different basis sets, are listed. TQZ denotes the TQ extrapolation scheme with the basis sets described in Table I, while QZ and TZ are the corresponding basis sets for the extrapolation. LP is the 6-311++G(3df,3pd) basis set.

System	TQZ	QZ	TZ	LP
G3/99 (223)	1.43	2.41	6.29	4.99
IP (40)	1.57	2.04	2.95	2.19
EA (25)	1.42	1.46	1.65	2.39
PA (8)	1.19	0.99	1.13	1.12
NHTBH (38)	1.29	1.33	1.53	1.42
HTBH (38)	0.65	0.63	0.70	0.71
S22 (22)	0.26	0.29	0.56	0.37
All (394)	1.29	1.89	4.23	3.44

puted by various density functionals. This test set can be regarded as a very stringent test, as it contains third-row elements (none is in our training set), and the accuracy of density functionals for AEs is usually very sensitive to their functional forms. As can be seen in Table IX, all of our  $\omega$ B97 types of functionals, B2PLYP-D and B2PLYP perform noticeably better than SCS-MP2 and MP2. This shows the importance of hybrid methods. Relative to B2PLYP-D,  $\omega$ B97X and  $\omega$ B97X-D, which are the best performing existing functionals, the performance of  $\omega$ B97X-2 is generally similar, but not superior.

We also test their performance on 30 reaction energies taken from NHTBH38 and HTBH38 with unequal forward and reverse barriers. These involve lighter elements than are in the G3/05 test set. As can be seen in Table X, all the functionals perform very well, with far smaller errors than MP2. For these molecules, the new LCDH functional,

TABLE IX. Statistical errors of the additional 48 AEs (in kcal/mol) in the G3/05 set (Ref. 52). The results for the  $\omega$ B97X-D are taken from Ref. 11, and the results for the  $\omega$ B97X and  $\omega$ B97 are taken from Ref. 10.

Error	$\omega$ B97X-2(LP)	$\omega$ B97X-D	$\omega$ B97X	$\omega$ B97	B2PLYP-D	B2PLYP	SCS-MP2	MP2
MSE	-0.36	0.24	0.76	1.28	-1.91	-2.87	-3.13	5.88
MAE	3.25	3.01	3.60	4.25	3.66	4.29	6.13	12.45
rms	4.57	3.95	4.52	5.41	4.60	5.88	8.32	18.37
Max (-)	-10.31	-6.28	-5.96	-6.50	-11.51	-18.56	-29.66	-20.39
Max (+)	20.64	13.06	14.88	18.14	10.84	10.15	15.97	61.56

$\omega$ B97X-2, and the existing DH functionals appear to perform somewhat better than the LC-DF methods. These results contrast with the what we observe for the G3/05 test set. Considering that PT2 correlation for noble gas atoms is known to change from underestimation to overestimation on going down the periodic table,<sup>54</sup> it appears that  $\omega$ B97X-2 may perform slightly better for the lighter elements on which it was trained. A similar comment may be made for B2PLYP and B2PLYP-D.

The performance of various functionals are examined on several sets of noncovalent interactions.<sup>43,53</sup> As can be seen in Table XI,  $\omega$ B97X-2 and  $\omega$ B97X-D perform similarly to the best method here, MP2. B2PLYP and SCS-MP2 perform less satisfactorily in this application. B2PLYP-D also performs very well here, though its performance is slightly inferior to both  $\omega$ B97X-D and  $\omega$ B97X-2. Considering that B2PLYP-D contains both empirical atom-atom dispersion interactions, and nonlocal PT2 correlation, it is encouraging

TABLE X. Comparison of errors of different functionals for the reaction energies (in kcal/mol) of the 30 chemical reactions in the NHTBH38/04 and HTBH38/04 database (Refs. 41 and 42). The results for the  $\omega$ B97X-D are taken from Ref. 11, and the results for the  $\omega$ B97X and  $\omega$ B97 are taken from Ref. 10.

Reactions	$\Delta E_{\text{ref}}$	$\omega$ B97X-2(LP)	$\omega$ B97X-D	$\omega$ B97X	$\omega$ B97	B2PLYP-D	B2PLYP	SCS-MP2	MP2
H+N <sub>2</sub> O→OH+N <sub>2</sub>	-65.08	2.09	4.80	3.72	3.82	5.16	5.13	4.35	12.81
H+FCH <sub>3</sub> →HF+CH <sub>3</sub>	-26.64	0.86	2.18	3.37	4.27	0.56	0.49	1.79	2.55
H+F <sub>2</sub> →HF+F	-103.91	-2.21	-0.70	0.50	2.21	-1.64	-1.64	-2.47	-1.50
CH <sub>3</sub> +FCl→CH <sub>3</sub> F+Cl	-52.74	-1.69	-1.02	-1.85	-2.60	-1.56	-1.50	-4.23	-3.70
F <sup>-</sup> +CH <sub>3</sub> Cl→FCH <sub>3</sub> +Cl <sup>-</sup>	-32.65	0.65	-2.18	-1.29	0.78	-0.99	-1.04	0.30	1.67
F <sup>-</sup> ⋯CH <sub>3</sub> Cl→FCH <sub>3</sub> ⋯Cl <sup>-</sup>	-26.73	1.49	-0.80	-0.23	1.17	0.76	0.73	0.35	1.74
OH <sup>-</sup> +CH <sub>3</sub> F→HOCH <sub>3</sub> +F <sup>-</sup>	-20.11	-0.07	-1.25	-1.22	-1.80	0.21	0.44	0.78	0.43
OH <sup>-</sup> ⋯CH <sub>3</sub> F→HOCH <sub>3</sub> ⋯F <sup>-</sup>	-36.24	-0.72	-2.44	-1.62	-1.36	-0.94	-0.93	-0.03	-1.38
H+N <sub>2</sub> →HN <sub>2</sub>	3.97	1.03	-5.06	-4.30	-3.57	-2.36	-2.35	14.34	15.02
H+CO→HCO	-19.51	-1.30	-3.28	-2.66	-1.91	-2.81	-2.77	3.01	2.74
H+C <sub>2</sub> H <sub>4</sub> →CH <sub>3</sub> CH <sub>2</sub>	-40.03	-1.95	-2.47	-2.97	-3.52	-0.95	-0.68	1.98	2.80
CH <sub>3</sub> +C <sub>2</sub> H <sub>4</sub> →CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub>	-26.12	-2.13	-2.90	-4.05	-5.65	-0.24	0.91	-0.33	-2.53
HNC→HNC	15.05	0.99	-1.85	-1.87	-1.97	0.34	0.31	1.83	2.35
H+HCl→H <sub>2</sub> +Cl	-3.0	1.63	2.71	3.09	3.18	0.40	0.40	1.87	6.23
OH+H <sub>2</sub> →H+H <sub>2</sub> O	-16.1	-0.54	-0.41	-0.84	-1.02	0.46	0.47	-2.99	-8.50
CH <sub>3</sub> +H <sub>2</sub> →H+CH <sub>4</sub>	-3.2	-0.17	-1.33	-2.30	-2.86	0.58	0.65	-1.35	-3.80
OH+CH <sub>4</sub> →CH <sub>3</sub> +H <sub>2</sub> O	-12.9	-0.37	0.92	1.46	1.84	-0.12	-0.18	-1.65	-4.70
OH+NH <sub>3</sub> →H <sub>2</sub> O+NH <sub>2</sub>	-9.5	-0.76	-0.17	0.15	0.23	-0.75	-0.79	-1.51	-2.71
HCl+CH <sub>3</sub> →Cl+CH <sub>4</sub>	-6.2	1.45	1.38	0.79	0.33	0.98	1.05	0.52	2.43
OH+C <sub>2</sub> H <sub>6</sub> →H <sub>2</sub> O+C <sub>2</sub> H <sub>5</sub>	-16.5	-0.28	0.22	0.54	1.04	-0.27	-0.58	-0.79	-4.06
F+H <sub>2</sub> →HF+H	-31.6	-1.33	-1.09	-1.46	-1.96	-0.47	-0.47	-3.65	-10.11
O+CH <sub>4</sub> →OH+CH <sub>3</sub>	5.6	-1.50	-0.92	-0.50	0.03	-1.82	-1.89	-0.48	-1.21
H+PH <sub>3</sub> →PH <sub>2</sub> +H <sub>2</sub>	-20.1	-0.62	-0.09	0.61	0.74	-1.75	-2.07	-0.40	1.56
H+HO→H <sub>2</sub> +O	-2.4	1.67	2.26	2.80	2.82	1.24	1.24	1.82	5.01
H+H <sub>2</sub> S→H <sub>2</sub> +HS	-13.8	0.93	1.60	2.17	2.32	-0.39	-0.50	1.15	4.35
O+HCl→OH+Cl	-0.6	-0.04	0.46	0.29	0.36	-0.84	-0.84	0.05	1.22
NH <sub>2</sub> +CH <sub>3</sub> →CH <sub>4</sub> +NH	-14.4	1.79	1.53	1.49	1.28	2.52	2.56	1.58	1.31
NH <sub>2</sub> +C <sub>2</sub> H <sub>5</sub> →C <sub>2</sub> H <sub>6</sub> +NH	-10.8	1.70	2.23	2.41	2.08	2.66	2.97	0.72	0.67
C <sub>2</sub> H <sub>6</sub> +NH <sub>2</sub> →NH <sub>3</sub> +C <sub>2</sub> H <sub>5</sub>	-7.0	0.48	0.39	0.39	0.81	0.48	0.21	0.72	-1.35
NH <sub>2</sub> +CH <sub>4</sub> →CH <sub>3</sub> +NH <sub>3</sub>	-3.3	0.29	0.99	1.21	1.50	0.53	0.51	-0.24	-2.09
MSE		0.05	-0.21	-0.07	0.09	-0.03	-0.01	0.57	0.58
MAE		1.09	1.66	1.74	1.97	1.16	1.21	1.91	3.75
rms		1.27	2.06	2.10	2.36	1.57	1.61	3.22	5.11
Max (-)		-2.21	-5.06	-4.30	-5.65	-2.81	-2.77	-4.23	-10.11
Max (+)		2.09	4.80	3.72	4.27	5.16	5.13	14.34	15.02



TABLE XI. Binding energies (in kcal/mol) of several sets of noncovalent interactions. The first three sets are taken from Ref. 53 with monomer deformation energies taken into considerations. The last three sets are taken from Ref. 43 without considering monomer deformation energies. The counter-point corrections are applied for all the cases. The results for the  $\omega$ B97X-D are taken from Ref. 11, and the results for the  $\omega$ B97X and  $\omega$ B97 are taken from Ref. 10.

Complex	$\Delta E_{\text{ref}}$	$\omega$ B97X-2(LP)	$\omega$ B97X-D	$\omega$ B97X	$\omega$ B97	B2PLYP-D	B2PLYP	SCS-MP2	MP2
Charge-transfer complexes									
C <sub>2</sub> H <sub>4</sub> ···F <sub>2</sub>	1.06	1.37	0.78	1.03	1.09	1.54	1.03	0.81	1.19
NH <sub>3</sub> ···F <sub>2</sub>	1.81	2.05	1.50	1.93	1.98	2.35	2.02	1.26	1.60
C <sub>2</sub> H <sub>2</sub> ···ClF	3.81	4.32	3.66	4.43	4.50	3.95	3.45	2.59	3.73
HCN···ClF	4.86	5.56	4.21	5.32	5.42	4.89	4.66	4.09	4.92
NH <sub>3</sub> ···Cl <sub>2</sub>	4.88	5.25	4.81	5.18	4.89	5.36	4.93	3.59	4.50
H <sub>2</sub> O···ClF	5.36	5.96	5.18	6.16	6.21	5.61	5.27	4.21	4.95
NH <sub>3</sub> ···ClF	10.62	11.53	11.12	11.10	10.49	12.29	11.69	8.45	10.33
MSE		0.52	-0.16	0.39	0.31	0.51	0.09	-1.06	-0.17
MAE		0.52	0.31	0.40	0.35	0.51	0.29	1.06	0.22
Dipole-dipole interaction complexes									
H <sub>2</sub> S···H <sub>2</sub> S	1.66	1.83	1.54	1.99	1.99	1.48	1.05	1.06	1.52
HCl···HCl	2.01	2.06	1.69	2.30	2.33	1.76	1.34	1.21	1.68
H <sub>2</sub> S···HCl	3.35	3.56	3.38	3.90	3.93	3.30	2.84	2.42	3.15
CH <sub>3</sub> Cl···HCl	3.55	3.54	3.17	3.82	3.97	3.26	2.43	2.25	3.07
HCN···CH <sub>3</sub> SH	3.59	3.87	3.72	3.99	4.05	3.67	2.89	2.83	3.46
CH <sub>3</sub> SH···HCl	4.16	5.01	4.87	5.28	5.38	4.85	3.94	3.48	4.61
MSE		0.26	0.01	0.50	0.56	0.00	-0.64	-0.85	-0.14
MAE		0.26	0.28	0.50	0.56	0.26	0.64	0.85	0.29
Weak interaction complexes									
He···Ne	0.04	0.06	0.00	0.01	-0.05	0.03	-0.01	0.00	0.01
He···Ar	0.06	0.10	0.00	0.05	-0.03	0.01	-0.03	0.00	0.02
Ne···Ne	0.08	0.08	-0.02	-0.02	-0.07	0.10	0.01	-0.01	0.00
Ne···Ar	0.13	0.15	-0.01	0.05	-0.04	0.12	-0.01	0.00	0.04
CH <sub>4</sub> ···Ne	0.22	0.22	0.13	0.10	0.00	0.18	0.00	0.04	0.08
C <sub>6</sub> H <sub>6</sub> ···Ne	0.47	0.51	0.24	0.30	0.32	0.46	-0.04	0.07	0.26
CH <sub>4</sub> ···CH <sub>4</sub>	0.51	0.73	0.60	0.64	0.55	0.42	-0.13	0.20	0.40
MSE		0.05	-0.08	-0.05	-0.12	-0.03	-0.24	-0.17	-0.10
MAE		0.05	0.11	0.09	0.13	0.03	0.24	0.17	0.10
Hydrogen-bonded DNA base pairs									
G···A HB	-11.30	-12.94	-13.48	-12.29	-12.44	-13.43	-10.75	-10.68	-12.85
C···G WC	-30.70	-31.49	-32.45	-31.92	-32.12	-32.10	-29.11	-27.62	-30.37
G···C WC	-31.40	-31.44	-32.28	-31.85	-32.07	-31.96	-29.03	-27.62	-30.32
MSE		-0.82	-1.60	-0.89	-1.08	-1.36	1.50	2.49	-0.05
MAE		0.82	1.60	0.89	1.08	1.36	1.50	2.49	0.99
Interstrand base pairs									
G···G IS	-5.20	-5.31	-5.43	-4.83	-4.70	-5.15	-4.24	-4.74	-5.17
G···G IS	0.80	0.67	1.15	2.21	2.13	1.14	3.13	1.21	0.08
C···C IS	3.10	3.21	3.29	3.62	3.69	3.18	3.35	3.06	2.92
MSE		-0.05	0.10	0.77	0.80	0.16	1.18	0.28	-0.29
MAE		0.12	0.25	0.77	0.80	0.16	1.18	0.30	0.31
Stacked base pairs									
A···G S	-6.50	-6.78	-6.66	-3.46	-4.62	-6.35	-0.63	-5.29	-8.61
C···G S	-12.40	-11.10	-10.83	-8.57	-9.61	-10.38	-5.55	-9.37	-12.07
G···C S	-11.60	-10.93	-11.06	-8.77	-9.69	-10.40	-5.77	-9.19	-11.70
MSE		0.56	0.65	3.23	2.19	1.12	6.19	2.22	-0.63
MAE		0.16	0.76	3.23	2.19	1.12	6.19	2.22	0.85
MSE		0.16	-0.14	0.51	0.36	0.11	0.75	0.04	-0.19
MAE		0.37	0.43	0.73	0.65	0.46	1.18	0.99	0.36
rms		0.55	0.68	1.18	0.93	0.76	2.16	1.39	0.59

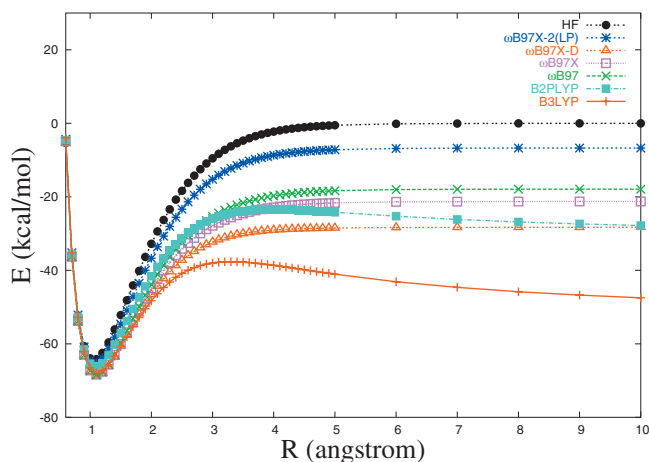


FIG. 1. Dissociation curve of  $H_2^+$  curve. Zero level is set to  $E(H)+E(H^+)$  for each method.

that  $\omega B97X-2$  (which does not contain the atom-atom interactions) achieves slightly better results on intermolecular interactions.

Common semilocal functionals are generally accurate for systems near equilibrium. However, due to considerable SIEs in semilocal functionals, spurious fractional charge dissociation occurs.<sup>7,8</sup> This situation becomes amplified for symmetric charged radicals  $X_2^+$ , such as  $H_2^+$ ,  $He_2^+$ ,  $Ne_2^+$ , and  $Ar_2^+$ . To test the extent to which LCDH methods improve upon the SIE problem, we performed unrestricted calculations with the aug-cc-pVQZ basis set and a high-quality EML(250,590) grid. The DFT results are compared with results from HF theory, MP2 theory, and the very accurate CCSD(T) theory.<sup>55,56</sup>

As shown in Fig. 1, the predicted  $H_2^+$  binding energy of  $\omega B97X-2(LP)$  is very close to the HF (exact) curve, and all the LC hybrids predict no spurious barriers on the dissociation curves. It appears that the SIE associated with  $\omega B97X-2(LP)$  is more than two times smaller than the next best DFT method shown. From Fig. 2,  $\omega B97X-2(LP)$  greatly improves upon the LC hybrids and B2PLYP for the  $He_2^+$  binding energy curve. Finally, for larger cations, such as  $Ne_2^+$  and  $Ar_2^+$ ,  $\omega B97X-2(LP)$  can dissociate them correctly (see

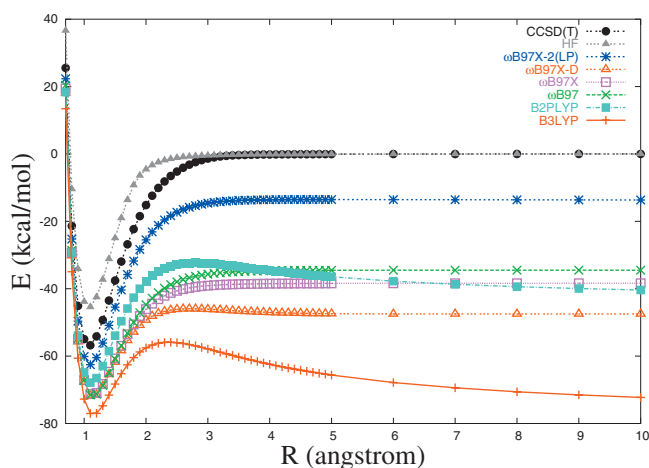


FIG. 2. Dissociation curve of  $He_2^+$  curve. Zero level is set to  $E(He)+E(He^+)$  for each method.

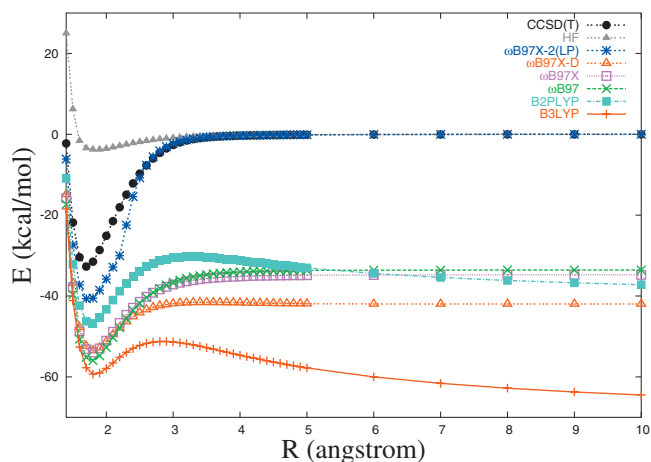


FIG. 3. Dissociation curve of  $Ne_2^+$  curve. Zero level is set to  $E(Ne)+E(Ne^+)$  for each method.

Figs. 3 and 4). This is a very encouraging result, which shows the value of the LCDH approach. The errors of cation binding energy curves at dissociation are summarized in Table XII, and quantify the significant improvements seen with  $\omega B97X-2(LP)$ .

However, all is not entirely well with the  $\omega B97X-2(LP)$  LCDH potential curves. Inspection of Figs. 3 and 4 shows that there is a discontinuity (also see Figs. 5 and 6) in the derivative of  $\omega B97X-2(LP)$  binding energy curves for  $Ne_2^+$  and  $Ar_2^+$ . There is a similar problem for MP2. This problem arises because the post-KS (or post-HF) PT2 correction causes the Hellman–Feynman theorem to no longer hold. The energy derivative therefore depends on the derivative of the orbitals, which can change discontinuously when the orbital Hessian exhibits a zero eigenvalue, such as at a spin-unrestriction point, or, as in this case, at the point where left-right symmetry-breaking occurs. These issues, including a related violation of N-representability have been discussed in detail elsewhere.<sup>57</sup> This undesirable property can, however, be removed by orbital-optimized (OO) methods.<sup>58</sup> It thus appears desirable to pursue OO-DH and OO-LCDH approaches in the future, although they will necessarily be somewhat more costly.

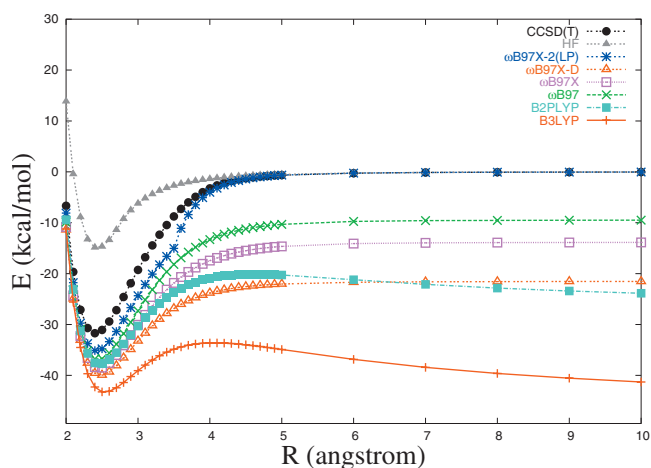


FIG. 4. Dissociation curve of  $Ar_2^+$  curve. Zero level is set to  $E(Ar)+E(Ar^+)$  for each method.

TABLE XII. Binding energies of symmetric radical cations at bond length  $R=100$  (Å),  $E_b=E[X_2^+,R=100(\text{Å})]-E(X)-E(X^+)$  (in kcal/mol). The results for the  $\omega$ B97X and  $\omega$ B97 are taken from Ref. 10.

Molecule	$\omega$ B97X-2(LP)	$\omega$ B97X-D	$\omega$ B97X	$\omega$ B97	B2PLYP	B3LYP
$H_2^+$	-6.7	-28.3	-21.3	-17.9	-31.3	-53.5
$He_2^+$	-13.8	-47.5	-38.4	-34.5	-44.0	-78.2
$Ne_2^+$	-0.0	-42.0	-34.7	-33.6	-41.0	-70.5
$Ar_2^+$	-0.0	-21.5	-13.8	-9.5	-27.6	-47.3

#### IV. CONCLUSIONS

We have developed a new LCDH functional based on our previous work.<sup>10</sup> This functional, called  $\omega$ B97X-2, includes 100% LR exact exchange, a large fraction (about 65 percent) of SR exact exchange, a modified B97 exchange density functional for SR interaction, the B97 correlation density functional,<sup>20</sup> and spin-component scaled PT2 correlations. There are a total of 16 parameters that must be specified, and we have done this by fitting to a large training set containing more than 400 pieces of data.

Since  $\omega$ B97X-2 is a parameterized functional, we also test it against MP2,<sup>34</sup> three well-established existing DH functionals [B2PLYP,<sup>29</sup> B2PLYP-D,<sup>30</sup> and SCS-MP2 (Ref. 49)] as well as our previous LC hybrid functionals ( $\omega$ B97,  $\omega$ B97X, and  $\omega$ B97X-D) on a separate independent test set of data, which includes further AEs, reaction energies, noncovalent interaction energies, and 4 symmetrical radical cations. The results indicate that this new LCDH functional is generally comparable or superior in performance for demanding cases such as AEs and base-stacking interactions. All the LC hybrid functionals are dramatically superior for radical cation problems that are sensitive to self-interaction errors, and  $\omega$ B97X-2 significantly improves upon the best of them.

As with all approximate density functionals, some limitations remain, and should be clearly laid out. First, while  $\omega$ B97X-2 is free of LR self-interaction, it still suffers from some self-interaction at SR, which means that its performance for the demanding problems of radical cations still

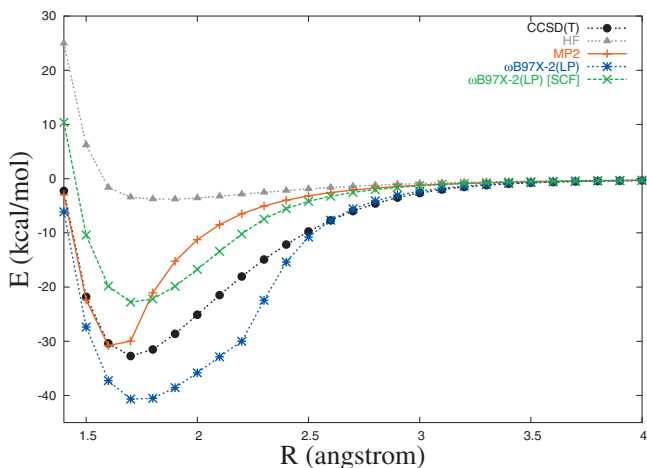


FIG. 5. Same as Fig. 3, but with a focus on the unrestricted region.

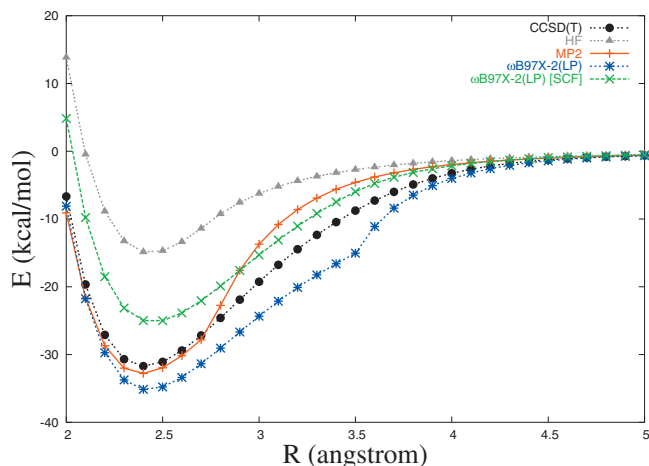


FIG. 6. Same as Fig. 4, but with a focus on the unrestricted region.

shows errors relative to truly self-interaction free methods. Second, because the fraction of exact exchange is significantly increased relative to semilocal functionals, the performance of  $\omega$ B97X-2 for systems with small gaps and thus potentially strong “static” correlation effects may be poorer than existing functionals. In general  $\omega$ B97X-2 is likely to be most suitable for applications to lighter elements. Third, LR correlation effects are solely treated by a post-KS treatment of the nonlocal correlation effects in  $\omega$ B97X-2, meaning that the KS orbitals are not affected by such corrections, which can cause problems (as seen in the  $Ne_2^+$  and  $Ar_2^+$  potential curve discontinuities). Orbital optimization would resolve these issues. Fourth, due to the use of wave function PT2 correlation,  $\omega$ B97X-2 is more sensitive to the choices of basis set than normal density functionals, which increases the computational cost for high-quality calculations. This problem can be reduced by using dual-basis methods<sup>59–61</sup> or R12 methods.<sup>62</sup>

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