

# Employing Range Separation on the meta-GGA Rung: New Functional Suitable for Both Covalent and Noncovalent Interactions

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We devise a scheme for converting an existing exchange functional into its range-separated hybrid variant. The underlying exchange hole of the Becke-Roussel type has the exact second-order expansion in the interelectron distance. The short-range part of the resulting range-separated exchange energy depends on the kinetic energy density and the Laplacian even if the base functional lacks the dependence on these variables. The most successful practical realization of the scheme, named LC-PBETPSS, combines the range-separated PBE exchange lifted to the hybrid meta-GGA rung and the TPSS correlation. The value of the range-separation parameter is estimated theoretically and confirmed by empirical optimization. The D3 dispersion correction is recommended for all energy computations employing the presented functional. Numerical tests show remarkably robust performance of the method for noncovalent interaction energies, barrier heights, main-group thermochemistry, and excitation energies.

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## I. INTRODUCTION

Since the seminal works of Becke,<sup>1,2</sup> it is known that the inclusion of the Hartree-Fock (HF) exchange in density-functional models not only moves practical DFT toward the goal of chemical accuracy in thermochemistry, but also has a theoretical justification rooted in the analysis of the exchange holes in molecular systems.<sup>3</sup> There are currently two prevalent ways of including the exact exchange in approximate DFT: as a fraction of the full HF exchange or as a long-range exact exchange component enabled only at long interelectron distances. The functionals built using the former approach, global hybrids, have become a staple of computational chemistry owing to their favorable trade-off between accuracy and cost.<sup>1,2,4</sup> However, the inclusion of only a fraction of the orbital exchange results in merely a slight correction of the self-interaction error inherited from the pure semilocal predecessors of global hybrids. To correct this deficiency, in range-separated (long-range corrected) hybrids the 100% HF exchange is introduced at long range. This way, the exact  $-1/R$  behavior of the exchange potential is forced upon approximate potentials.<sup>5,6</sup> At the same time, range separation avoids the use of the full orbital exchange at all distances, which would be incompatible with an approximate semilocal correlation.

Range-separated hybrids are free from a number of shortcomings arising as a consequence of the self-interaction error. The correct long-range potential of a range-separated hybrid exchange makes the HOMO energy close to the vertical ionization energy,<sup>7,8</sup> approximately satisfying Janak's theorem.<sup>9</sup> The spurious propensity to transfer electrons is reduced, which improves the description of donor-acceptor systems with partial charge transfer in ground and excited states. The inclusion of the long-range exact exchange also corrects the underestimation of Rydberg excitation energies and oscillator strengths,<sup>10</sup> and corrects the overestimation of longitudinal (hyper)polarizabilities of polyenes.<sup>11</sup>

The majority of the available range-separated functionals are hybrids based on the generalized gradient approximation (GGA).<sup>10,12-19</sup> Notably, a systematic search spanning the vast space of possible mathematical forms have been conducted to find range-separated GGAs with the best general performance.<sup>20</sup> In contrast, only a few attempts have been made to develop a range-separated meta-GGA functional, i.e., a hybrid model in which the semilocal part depends not only on the density and density gradient, but also on the kinetic energy density and in some cases the Laplacian. Empirical functionals of this kind have been pro-

posed by Lin et al.<sup>21,22</sup> ( $\omega$ M05-D and  $\omega$ M06-D3) and by Peverati et al.<sup>23</sup> (M11). While these methods are heavily parametrized, e.g., M11 contains 40 empirical parameters, the available tests show that the improvement over the best range-separated GGAs is nonuniform and minor.<sup>22,24</sup> A nonempirical range-separated meta-GGA based on the TPSS functional was tested by Vydrov et al.,<sup>5</sup> but for thermochemistry this method showed no improvement over the pure TPSS functional.

The purpose of this work is to construct a reliable range-separated functional in which the short-range exchange part is a meta-GGA derived from an existing nonempirical semilocal model.

The range-separated exchange energy consists of two components, short-range and long-range, defined according to the range split of the electron interaction,

$$\frac{1}{s} = \frac{\operatorname{erfc}(\omega s)}{s} + \frac{\operatorname{erf}(\omega s)}{s}, \quad (1)$$

where  $\omega$  is the range separation parameter and  $s = |\mathbf{r}_1 - \mathbf{r}_2|$ . Inserting Eq. 1 into the definition of the exchange energy yields the formulae for the short-range and long-range components:

$$E_{X,\text{approx}}^{\text{SR}} = \frac{1}{2} \sum_{\sigma} \iint \frac{\rho_{\sigma}(\mathbf{r}_1) h_{X,\text{approx}}^{\sigma}(\mathbf{r}_1, \mathbf{r}_2) \operatorname{erfc}(\omega s)}{s} d^3\mathbf{r}_1 d^3\mathbf{r}_2, \quad (2)$$

$$E_{X,\text{exact}}^{\text{LR}} = \frac{1}{2} \sum_{\sigma} \iint \frac{\rho_{\sigma}(\mathbf{r}_1) h_{X,\text{exact}}^{\sigma}(\mathbf{r}_1, \mathbf{r}_2) \operatorname{erf}(\omega s)}{s} d^3\mathbf{r}_1 d^3\mathbf{r}_2. \quad (3)$$

The long-range exchange energy  $E_{X,\text{exact}}^{\text{LR}}$  is based on the exact, orbital-dependent HF exchange hole

$$h_{X,\text{exact}}^{\sigma}(\mathbf{r}_1, \mathbf{r}_2) = - \frac{\left| \sum_i^{N_{\sigma}} \psi_{i\sigma}^*(\mathbf{r}_1) \psi_{i\sigma}(\mathbf{r}_2) \right|^2}{\rho_{\sigma}(\mathbf{r}_1)}. \quad (4)$$

In the definition of the short-range exchange energy  $E_{X,\text{approx}}^{\text{SR}}$ , one has to assume a specific form of the approximate exchange hole  $h_{X,\text{approx}}^{\sigma}$ . As in the case of the exchange energy density, the local definition of the exchange hole is not unique. However, the ambiguity disappears in the system average of the hole.<sup>25</sup>

In what follows, we present equations for closed-shell systems with  $\rho_{\alpha} = \rho_{\beta} = \rho/2$ . There is no loss of generality because the exchange functional for arbitrary spin polarizations is simply related to its spin-compensated counterpart by the formula<sup>26</sup>

$$E_X[\rho_{\alpha}, \rho_{\beta}] = \frac{1}{2} E_X[2\rho_{\alpha}] + \frac{1}{2} E_X[2\rho_{\beta}]. \quad (5)$$

For clarity, hereafter we skip the spin index in the exchange hole symbol.

There exists a series of range-separated GGAs which employ various levels of exact constraints in the model exchange hole inserted into the definition of  $E_X^{\text{SR}}$ .

One of the earliest range-separated functionals are those of Iikura, Tsuenda, Yanai, and Hirao (ITYH),<sup>27</sup> who devised a general technique of converting existing GGAs into range-separated hybrids. The ITYH scheme was employed in several functionals, including LC-BLYP, LC-BOP, LC-PBEOP, and CAM-B3LYP.<sup>10,12,13</sup>

The ITYH exchange hole is based on a simple modification of the LDA exchange hole.<sup>27</sup> It has the correct value at  $s = 0$ ,

$$h_{X,\text{ITYH}}(\mathbf{r}_1, s = 0) = h_{X,\text{exact}}(\mathbf{r}_1, s = 0) = -\frac{\rho(\mathbf{r}_1)}{2}, \quad (6)$$

and satisfies the energy integral

$$\frac{1}{2} \int \frac{h_{X,\text{ITYH}}(\mathbf{r}_1, s)}{s} 4\pi s^2 ds = \epsilon_{X,\text{approx}}(\mathbf{r}_1), \quad (7)$$

where  $\epsilon_{X,\text{approx}}$  is the exchange energy density of a given base functional. The ITYH hole fails to fulfill two other exact conditions appropriate to a semilocal functional: the hole normalization<sup>14</sup>

$$\int h_{X,\text{exact}}(\mathbf{r}_1, s) 4\pi s^2 ds = -1 \quad (8)$$

and the correct second-order short-range expansion of the spherically-averaged exchange hole at zero current density,<sup>28-30</sup>

$$h_{X,\text{exact}}(\mathbf{r}_1, s) = -\frac{\rho}{2} - Qs^2 + \dots, \quad (9)$$

$$Q = \frac{1}{12} \nabla^2 \rho - \frac{1}{6} \tau + \frac{1}{24} \frac{(\nabla \rho)^2}{\rho}, \quad (10)$$

where  $\tau$  is the kinetic energy density

$$\tau = 2 \sum_{i=1}^{N_{\text{orb}}} |\nabla \psi_i|^2. \quad (11)$$

It should be stressed that Eq. 10 cannot be satisfied at the GGA level.

Several GGAs have been developed in which the exchange hole obeys more exact conditions than the ITYH model. The range-separated PBE functionals of Henderson et al.<sup>14</sup> and of Vydrov et al.<sup>15</sup> satisfy Eq. 6, Eq. 7, Eq. 8, and only approximately Eq. 10. Both methods improve over the ITYH model in atomization energies and barrier heights.<sup>14</sup>

Still, there is a possibility for going one rung higher than the existing range-separated GGAs. This work presents a scheme for construction of meta-GGA range-separated exchange functionals which employ the kinetic energy density and the Laplacian to exactly include the second-order coefficient of Eq. 10. The method allows one to transform an existing GGA or a meta-GGA model into its range separated variant. The resulting functional depends on the kinetic energy density and the Laplacian even if the base functional does not.

In the following, we begin by deriving the working equations of the new range-separation scheme. Next, we search for a preferred combination of the base exchange functional and the accompanying correlation model. Finally, we test the performance of the selected functional on a test set including thermochemical energy differences, barrier heights, noncovalent interaction energies, and excitation energies.

## II. THEORY

### A. Exchange Hole Model

Our range-separation scheme requires an exchange hole model which integrates to  $\epsilon_{X,\text{approx}}$  and has enough degrees of freedom to satisfy two further conditions: the exact value of  $h_{X,\text{approx}}$  at  $s = 0$  and the exact coefficient of  $s^2$ . These prerequisites are satisfied by the generalized Becke-Roussel (BR) exchange hole.<sup>31,32</sup> The spherically-averaged generalized BR hole,

$$h_{X,\text{BR}}(a, b, \mathcal{N}; s) = -\mathcal{N} \frac{a}{16\pi bs} \left[ (a|b - s| + 1)e^{-a|b-s|} - (a|b + s| + 1)e^{-a|b+s|} \right], \quad (12)$$

includes three parameters,  $a$ ,  $b$ , and  $\mathcal{N}$ , which we will define by selecting a subset of three equations from a wider set of possible conditions. For any  $a > 0$  and  $b > 0$ , the normalization integral of  $h_{X,\text{BR}}$  is

$$\int h_{X,\text{BR}}(a, b, \mathcal{N}; s) 4\pi s^2 ds = -\mathcal{N}. \quad (13)$$

In the original BR model, the parameters  $a$  and  $b$  are fixed by enforcing the zeroth- and second-order coefficients of Eq. 9, and the normalization is set to  $-1$ , i.e.,  $\mathcal{N} = 1$ . With these definitions satisfied, the original  $h_{X,\text{BR}}$  reduces to the exact exchange hole when applied to the hydrogen atom.<sup>31</sup>

The original definitions of the BR model have to be modified so that the electrostatic potential generated by  $h_{X,\text{BR}}$  corresponds to the assumed base exchange energy density:

$$\frac{1}{2} \int_0^\infty \frac{h_{X,\text{BR}}(a, b, \mathcal{N}; s)}{s} 4\pi s^2 ds = \epsilon_{X,\text{approx}}. \quad (14)$$

The formula for the short-range component of  $\epsilon_{X,\text{approx}}$  will be given in Section II B. Following Becke<sup>32</sup> and Precechtelova et al.,<sup>33</sup> we enforce Eq. 14 at the cost of relaxing the normalization condition. The set of equations defining the parameters of  $h_{X,\text{BR}}$ ,

$$\frac{x-2}{x^2} \left( e^x - 1 - \frac{x}{2} \right) = -\frac{6Q}{\pi\rho^2} \epsilon_{X,\text{approx}}, \quad (15)$$

$$a = \sqrt{\pi\rho \frac{(2 - 2e^x + x)}{x\epsilon_{X,\text{approx}}}}, \quad (16)$$

$$b = x/a, \quad (17)$$

$$\mathcal{N} = 4\pi\rho e^x/a^3, \quad (18)$$

is to be solved at each point of space. (For the derivation of Eqs. 15–18 see the Appendix of ref 32.) For any physically allowed right-hand side, a unique  $x > 0$  solves Eq. 15. The solution can be obtained with a numerical solver or interpolation.

The resulting exchange hole integrates to the given  $\epsilon_{X,\text{approx}}$  (Eq. 14), has the exact value at the origin (Eq. 6), and recovers the exact coefficient of  $s^2$  (Eq. 10). However, its normalization integral differs in general from the exact value of  $-1$ .

## B. Short-Range Exchange Energy

The short-range exchange energy density  $\epsilon_{X,\text{approx}}^{\text{SR}}$  is the difference between the full-range semilocal exchange and its long-range part:

$$\epsilon_{X,\text{approx}}^{\text{SR}} = \epsilon_{X,\text{approx}} - \epsilon_{X,\text{approx}}^{\text{LR}}. \quad (19)$$

We define  $\epsilon_{X,\text{approx}}^{\text{LR}}$  using the potential generated by  $h_{X,\text{BR}}$ :

$$\epsilon_{X,\text{approx}}^{\text{LR}} = \frac{1}{2} \int_0^\infty \frac{h_{X,\text{BR}}(s)\text{erf}(\omega s)}{s} 4\pi s^2 ds = \frac{1}{2} U_{X,\text{approx}}^{\text{LR}}. \quad (20)$$

The integration in Eq. 20 can be done analytically, giving

$$U_{X,\text{approx}}^{\text{LR}} = -\frac{\mathcal{N}\omega}{\nu} \text{erf}(\nu) \quad (21)$$

$$+ \frac{\mathcal{N}\omega}{2\nu} (1 - \mu^2 + \mu\nu) \text{erfc}(\mu - \nu) \exp(\mu^2 - 2\mu\nu) \\ + \frac{\mathcal{N}\omega}{2\nu} (-1 + \mu^2 + \mu\nu) \text{erfc}(\mu + \nu) \exp(\mu^2 + 2\mu\nu), \quad (22)$$

$$\mu = \frac{a}{2\omega}, \quad (23)$$

$$\nu = b\omega. \quad (24)$$

For small values of  $\nu$ , the right-hand side of Eq. 22 should be evaluated using a Taylor series expansion to avoid numerical errors. Finally, the short-range exchange energy is obtained by integrating  $\epsilon_{X,\text{approx}}^{\text{SR}}$  over the whole space:

$$E_{X,\text{approx}}^{\text{SR}} = \int \epsilon_{X,\text{approx}}^{\text{SR}}(\mathbf{r}_1) \rho(\mathbf{r}_1) d\mathbf{r}_1. \quad (25)$$

The complete range-separated exchange energy is the sum of  $E_{X,\text{approx}}^{\text{SR}}$  and the long-range HF exchange,

$$E_{X,\text{approx}} = E_{X,\text{approx}}^{\text{SR}} + E_{X,\text{exact}}^{\text{LR}}. \quad (26)$$

### C. One-Electron Self-Interaction Error

We use the example of the self-interaction error in the ground state of the hydrogen atom to illustrate the difference between our meta-GGA range-separation scheme and the existing GGA approaches.

The ground state of the hydrogen atom is a difficult limiting case for conventional DFT approximations. Using only local variables  $\rho(\mathbf{r}_1)$  and  $\nabla\rho(\mathbf{r}_1)$ , GGAs have no way of knowing that the density under consideration belongs to a single-particle system. Therefore, the one-electron self-interaction error arises as a residual value left by an imperfect cancellation between an approximate exchange energy and the Coulomb repulsion.<sup>31,36</sup> A single-electron density can be detected using the kinetic energy density  $\tau$ , thus meta-GGA functionals can, at least partially, reduce the self-interaction error.

The large- $\omega$  behavior of the exact short-range exchange energy of the hydrogen atom is given by the expansion<sup>37</sup>

$$E_{X,\text{exact}}^{\text{SR}}(\omega \rightarrow \infty) = -\frac{1}{16\omega^2} + \frac{1}{32\omega^4} + \dots \quad (27)$$

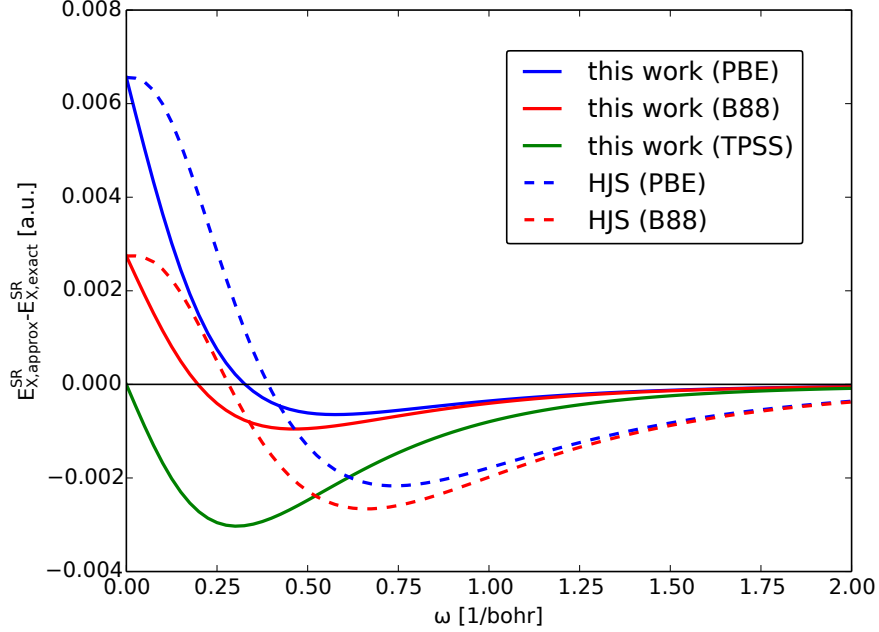


FIG. 1: Differences between approximate and exact short-range exchange energies of the ground state of the hydrogen atom. All computations employ the aug-cc-pV5Z basis set<sup>34</sup> and HF orbitals. The short-range GGA models of Henderson et al.<sup>14,35</sup> are denoted as HJS. Correlation energies are not included.

Eq. 27 assumes the exact density. Gill et al. have shown that the first term on the right-hand side is recovered already by the local density approximation, but the term of order  $1/\omega^4$  requires  $h_{X,\text{approx}}$  with the correct second-order expansion for small  $s$ .<sup>37</sup> Indeed, the short-range meta-GGA functionals derived in this work, which satisfy Eq. 10, approach  $E_{X,\text{exact}}^{\text{SR}}(\omega \rightarrow \infty)$  visibly faster than the existing GGAs (Figure 1). The reduction of errors for large  $\omega$  is seen for all tested base functionals: PBE,<sup>38</sup> B88,<sup>39</sup> and TPSS.<sup>40</sup>

Figure 2 shows why, in our scheme, TPSS is not a preferred candidate for the base exchange functional, and PBE should be used instead. Let  $\langle h_X \rangle(s)$  denote the system and spherical average of the exchange hole for the hydrogen atom,

$$\langle h_X \rangle(s) = \int \rho(\mathbf{r}_1) h_X(\mathbf{r}_1, s) d\mathbf{r}_1. \quad (28)$$

The real-space analysis of the total exchange energy is then expressed as

$$E_X = \int_0^\infty H_X^{\text{TOT}}(s) ds, \quad (29)$$

where

$$H_X^{\text{TOT}}(s) = 2\pi s \langle h_X \rangle(s), \quad (30)$$



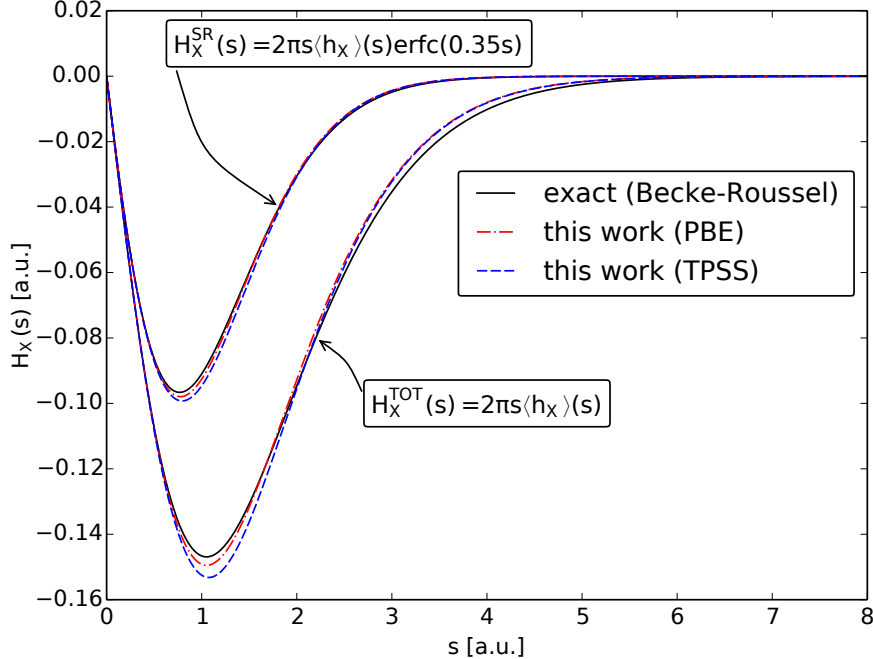


FIG. 2: Real-space analysis of the contributions to the (short-range) exchange energy of the hydrogen atom. All computations employ the aug-cc-pV5Z basis set<sup>34</sup> and HF orbitals.

and the short-range exchange energy is

$$E_X^{\text{SR}}(\omega) = \int_0^\infty H_X^{\text{SR}}(s) ds, \quad (31)$$

where

$$H_X^{\text{SR}}(s) = 2\pi s \langle h_X \rangle(s) \text{erfc}(\omega s). \quad (32)$$

For the TPSS exchange,  $H_X^{\text{TOT}}(s)$  is too deep around  $s = 1$  bohr and too shallow in the tail, but these two errors perfectly cancel each other to yield the exact  $E_X$  enforced by the construction of the TPSS exchange. However, the factor  $\text{erfc}(\omega s)$  included in the short-range energy cuts off the tail of  $H_X^{\text{TOT}}(x)$ , thus leaving the relatively large short-range error uncompensated in  $E_X^{\text{SR}}$ . By contrast, in the PBE energy, the short-range and long-range errors in  $H_X^{\text{TOT}}(s)$  do not cancel perfectly, but the error at short range is small, and the factor  $\text{erfc}(\omega s)$  enhances the error cancellation in  $E_X^{\text{SR}}$ .

The single-electron density of the hydrogen atom has been previously utilized as a constraint in the design of several functionals. The TPSS exchange of Tao et al.<sup>40</sup> and the MVS exchange of Sun et al.<sup>41</sup> are parametrized to recover the exact exchange energy in this

limit. The hydrogen atom energy is also included in the training set of the empirical M05-2X functional.<sup>42</sup> Here, we use the single-electron limit to estimate the value of  $\omega$  which is most appropriate for the range-separated exchange energy obtained using our scheme. According to Figure 1, our model of the short-range PBE exchange energy recovers the exact energy at  $\omega = 0.33$ . Later in the text we will show that this value is nearly optimal for the atomization energies and barrier heights of small molecules.

Apart from its manifestation in approximate exchange energy functionals, the self-interaction error arises as a nonvanishing correlation energy of a single-electron system. In the case of the pure PBE exchange-correlation functional, the total energy of the hydrogen atom is only 0.0006 a.u. lower than the exact energy, but at the same time the correlation contribution amounts to  $-0.006$  a.u. ( $-3.8$  kcal/mol). This error can be eliminated only at the meta-GGA level. The desired improvement over the PBE correlation is provided by TPSS.<sup>40,43</sup> The TPSS correlation is built on the PBE formula, but with one-electron self-interaction terms subtracted.<sup>43</sup> As a result, TPSS yields exactly zero correlation energy for the hydrogen atom, which we regard as a feature compatible with our exchange model. We will test the advantage of using the TPSS correlation over PBE for general systems in the following section.

#### D. Complete Exchange-Correlation Model

To fully define our exchange-correlation functional, we have to specify the base exchange functional together with the accompanying model for correlation. We restrict our search to two exchange-correlation models only: PBE and TPSS. The choice of these two functionals reflects our preference for methods with a small number of empirical parameters. Still, it remains possible to pair our range-separation scheme with formulae including multiple adjustable parameters and to perform a comprehensive empirical optimization.

Let LC-XY denote a range-separated functional where  $X$  is the base model for exchange ( $\epsilon_{X,\text{approx}}$  in Eq. 15), and  $Y$  is the accompanying correlation. Our search comprises three candidate functionals, LC-PBETPSS, LC-PBEPBE, and LC-TPSSTPSS, applied on a set of atomization energies (AE6<sup>44</sup>) and barrier heights (BH6<sup>44</sup>). Each functional is employed with a varying value of  $\omega$ . The best method is selected for further tests described in the remainder of this paper. The AE6 and BH6 benchmarks are representative of 109 atomization energies

and 44 barrier heights, respectively, in the Database/3 collection.<sup>44</sup>

LC-TPSSTPSS is the poorest performing functional, which cannot fully benefit from the addition of the long-range exact exchange. For this functional, a single value of  $\omega$  cannot work well for both AE6 and BH6: the optimal value for the former set is  $\omega=0.0$ , i.e., the limit of the pure TPSS functional, whereas for the latter set  $\omega=0.35$  minimizes the mean absolute error (MAE). A similar behavior of the TPSS range-separated hybrid has been observed by Vydrov et al.<sup>5</sup> The numerical data for LC-TPSSTPSS are available in the Supporting Information.

The problem of choosing a universally applicable value of  $\omega$  arises again in the case of the candidate based entirely on the PBE model, LC-PBEPBE, albeit it is not as severe as for LC-TPSSTPSS. At  $\omega = 0.30$ , the average error in the barrier heights is only 1.6 kcal/mol, but at the same time the error for the atomization energies is as high as 10.5 kcal/mol, which is large compared to the existing range-separated functionals.<sup>14</sup>

The best overall accuracy is achieved by LC-PBETPSS (Figure 3). The optimal range-separation parameter for this functional is in the interval  $0.30 \leq \omega \leq 0.35$ , depending on the weight of the BH6 set relative to AE6. (The percentage errors on the BH6 set are much larger than on AE6, see the Supporting Information.) This result matches our theoretical estimate,  $\omega = 0.33$ , based on the minimization of the self-interaction error for the hydrogen atom. Taking into account the relatively large errors in the barrier heights, we choose  $\omega = 0.35$  for the final version of LC-PBETPSS recommended for general use. The MAEs at this value of the range-separation parameter are 6.7 kcal/mol for AE6 and 2.1 kcal/mol for BH6. LC-PBETPSS is the final, recommended functional which we will employ in the full test set.

The long-range correction proposed here should not be confused with the correction based on the ITYH scheme, which can be applied, e.g., in the Gaussian program, to any pure functional. Let us denote by LC-PBETPSS(ITYH) a functional which employs the ITYH-based range-separated PBE exchange.<sup>27</sup> Using the above-described procedure for optimizing the range-separation parameter, we find that  $\omega = 0.7$  is optimal simultaneously for AE6 (MAE=14.7 kcal/mol) and BH6 (MAE=2.6 kcal/mol). For both sets, LC-PBETPSS(ITYH) is inferior to LC-PBETPSS, but the difference is especially large for the atomization energies. On the AE6 set, LC-PBETPSS(ITYH) is only slightly more accurate than the pure PBETPSS functional without any addition of the HF exchange. For  $0.20 \leq \omega \leq$

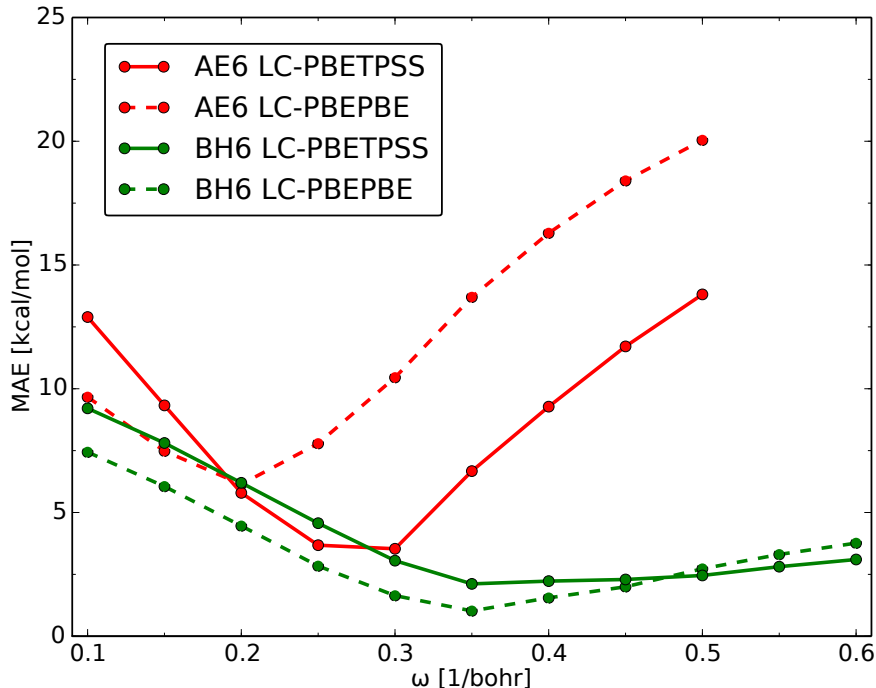


FIG. 3: Mean absolute errors on the AE6 and BH6 sets.<sup>44</sup> All DFT computations employ the def2-QZVPP basis set.<sup>34,45</sup> The reference values are taken from ref 4 (AE6) and ref 46 (BH6).

0.35, where LC-PBETPSS performs well for AE6, LC-PBETPSS(ITYH) yields extremely large MAEs above 30 kcal/mol. Alternatively, one could combine the range-separated PBE exchange of Henderson et al.<sup>14</sup> and the TPSS correlation to obtain LC-PBETPSS(HJS). While this method performs generally better than LC-PBETPSS(ITYH), for its optimal value of  $\omega = 0.45$ , the errors for AE6 (MAE=9.9 kcal/mol) and BH6 (MAE=2.4 kcal/mol) are both larger than for LC-PBETPSS. The numerical data for LC-PBETPSS(ITYH) and LC-PBETPSS(HJS) are available in the Supporting Information.

## E. Dispersion Correction

A dispersion correction compensates for the deficiencies of a semilocal DFT approximation in the modeling of long-range correlation contributions to noncovalent interaction energies. We test the performance of LC-PBETPSS with the D3 correction of Grimme et

al.<sup>47</sup> The general form of the atom-pairwise D3 correction is<sup>47</sup>

$$E_{\text{disp}}(\text{D3}) = - \sum_{A>B} \sum_{n=6,8} s_n \frac{C_6^{AB}}{R_{AB}^n} f_{\text{damp}}^{(n)}(R_{AB}), \quad (33)$$

$$f_{\text{damp}}^{(n)}(R_{AB}) = \frac{1}{1 + 6(R_{AB}/(r_n R_0^{AB}))^{-\alpha_n}}, \quad (34)$$

where  $f_{\text{damp}}^{(n)}$  is the damping function. The only functional-dependent parameters are  $r_6$  and  $s_8$ . The  $C_6^{AB}$  dipole-dipole coefficients are obtained ab initio, tabulated, and interpolated for the effective coordination numbers in the system of interest. The minimization of the MAE for LC-PBETPSS-D3 on the S22 set of noncovalent systems<sup>48,49</sup> for LC-PBETPSS yields  $r_6 = 0.88971$ . The  $1/R^8$  term is not included because it does not decrease the MAE for the training set ( $s_8 = 0$ ). We employ the original damping function  $f_{\text{damp}}^{(n)}(R_{AB})$ ,<sup>47</sup> which vanishes for  $R_{AB} \rightarrow 0$ , instead of the newer Becke-Johnson damping<sup>50</sup> to avoid double counting of the interaction energy at short range. Optionally, a 3-body term can be added to model the Axilrod-Teller-Muto contribution to the dispersion energy:<sup>47</sup>

$$E_{\text{disp}}^{\text{3-body}}(\text{D3}) = - \sum_{A>B>C} C_9^{ABC} \frac{(3 \cos \theta_a \cos \theta_b \cos \theta_c + 1)}{(R_{AB} R_{BC} R_{CA})^3} f_{\text{damp}}^{(9)}(\bar{R}_{ABC}), \quad (35)$$

where  $\theta_a$ ,  $\theta_b$ , and  $\theta_c$  are angles between the three interacting atoms, and  $\bar{R}_{ABC}$  is the geometric mean of the interatomic distances. The triple-dipole coefficient  $C_9^{ABC}$  is approximated as

$$C_9^{ABC} = -\sqrt{C_6^{AB} C_6^{AC} C_6^{BC}}. \quad (36)$$

The nonadditive 3-body term is known to be important for large systems.<sup>51</sup>

### III. RESULTS AND DISCUSSION

#### A. Electronic-Structure Methods

The functional developed in this work is denoted as LC-PBETPSS. For the clarity of presentation, let us list its main characteristics which were discussed in the previous sections. The range-separated exchange combines the meta-GGA short-range PBE exchange and the 100% HF exchange at long range. The range-separation parameter of the exchange is fixed at  $\omega = 0.35$ . The TPSS model is used for the correlation term. The LC-PBETPSS functional is applied with the D3 dispersion correction (LC-PBETPSS-D3) and for some systems without

the dispersion term (LC-PBETPSS). The LC-PBETPSS functional is implemented in the developer version of the Molpro program.<sup>52</sup>

To make a fair presentation of the performance of the new method, we have assembled a test set of well-established functionals for comparison. The LC- $\omega$ PBE functional of Vydrov and Scuseria<sup>15</sup> is a GGA range-separated functional based on the PBE exchange and PBE correlation. The numerical comparison between LC-PBETPSS-D3 and LC- $\omega$ PBE-D3 probes the cumulative effect of upgrading the short-range exchange to meta-GGA and removing the one-electron self-interaction error from the correlation. The M06-2X empirical meta-GGA functional of Zhao and Truhlar<sup>53</sup> is a workhorse of modern computational chemistry. Even though this functional reproduces a large part of the dispersion energy in the vicinity of equilibrium separations, adding the D3 correction slightly improves the results in general. M06-2X-D3 is the best dispersion-corrected meta-GGA hybrid on the GMTKN30 database.<sup>54</sup>  $\omega$ B97XD is an empirical, dispersion-corrected, range-separated GGA functional of Chai and Head-Gordon.<sup>18</sup> It is designed for thermochemistry, kinetics, and energies of noncovalent systems.  $\omega$ B97X<sup>17</sup> is a predecessor of  $\omega$ B97XD, which is not optimized for use with a dispersion correction. Still, its design makes it suitable for spectroscopic properties.<sup>55</sup> We employ  $\omega$ B97X in the part of our tests devoted to excitation energies. M06-L is an empirical meta-GGA functional which does not contain any HF exchange.<sup>53</sup> It is known for the reliable description of hydrogen-bonded systems.<sup>56</sup> Finally, B3LYP-D3 is an example of a hybrid functional<sup>57</sup> developed in the 1990s, supplemented with the modern D3 correction.

In addition to DFT methods, for ground-state charge-transfer dimers we use the DLPNO-CCSD(T) method,<sup>58</sup> which is a low-scaling approximation within the coupled-cluster wave function formalism including connected triples. The numerical thresholds for DLPNO-CCSD(T) are set at the “tight” level defined in Table 1 of ref 59, as recommended for noncovalent interactions.<sup>59</sup> The DLPNO-CCSD(T) computations are performed with the ORCA 3.0.3 program.<sup>60</sup>

## B. Hydrogen-Bonded Systems

Modeling of hydrogen-bonded clusters is still challenging for modern DFT procedures. Common hybrid GGAs and the M06-type functionals accurately describe the binding energies but unexpectedly fail for the proton-exchange barriers on the CEPX33 set of  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ ,

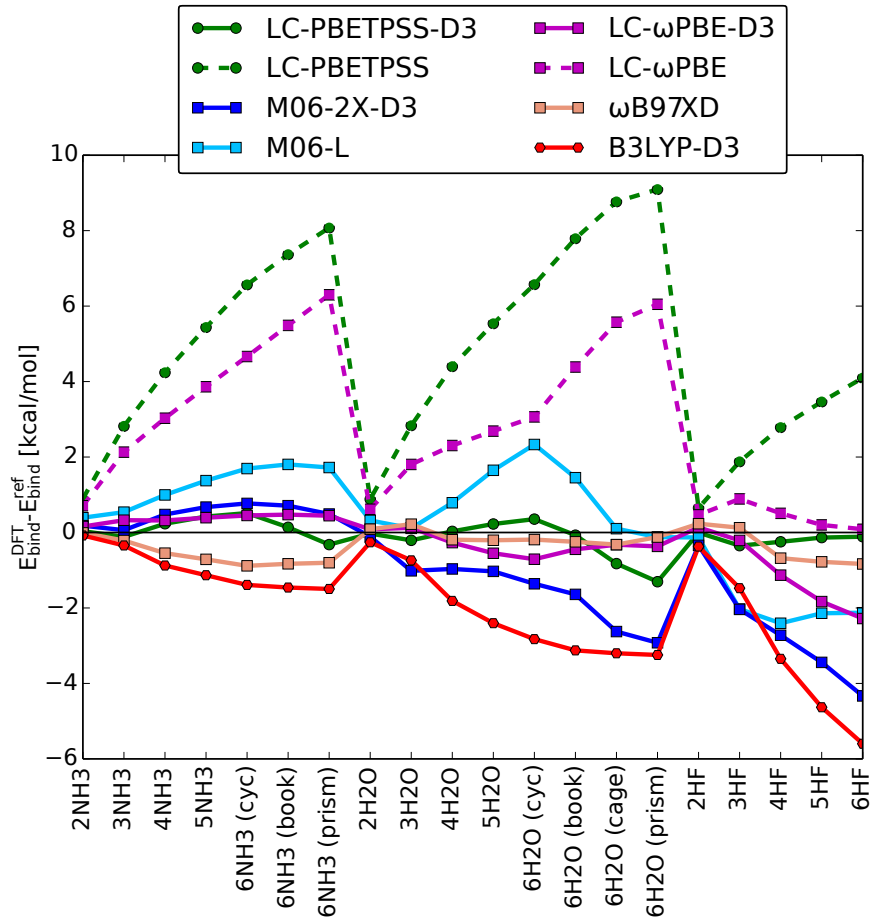


FIG. 4: Errors for the binding energies of the CEPX33 set. The computational details are provided in Table I.

and HF clusters.<sup>56,61</sup> In our tests on the CEPX33 set, LC-PBETPSS-D3 performs consistently well for both properties (Figs. 4 and 5). It is the best method for the binding energies and only slightly less accurate than the best functional (M06-L) for the barriers. The D3 correction added to LC-PBETPSS improves the results for both binding energies and barrier heights (Table I). This is in contrast to LC- $\omega$ PBE, for which the effect of supplying the dispersion term is inconsistent.

To test if the high accuracy of LC-PBETPSS-D3 persists for systems larger than those of the CEPX33 set, we apply this functional on the set of water 16-mers studied by Yoo et al.<sup>62</sup> Here, some of the water molecules are connected through hydrogen bonds to four nearest neighbors. The structures of kind I (4444-a and 4444-b) include eight such nodes, whereas the structures of kind II (antiboat, boat-a, and boat-b) include four water molecules with such high connectivity.<sup>62</sup> As illustrated in Figure 6, LC-PBETPSS-D3 represents reliably

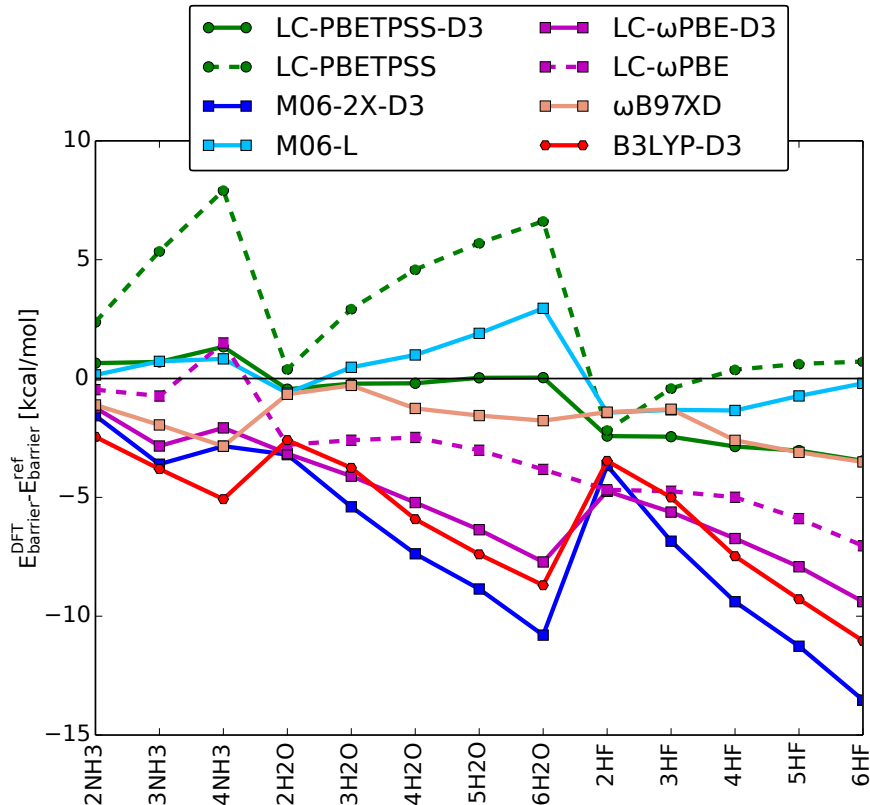


FIG. 5: Errors for the proton-exchange barriers of the CEPX33 set. The computational details are provided in Table I.

the absolute binding energies, but it predicts that the clusters of kind I are slightly too stable relative to the clusters of kind II. A similar, yet more pronounced error in the relative energies is present for the M06-type functionals: M06-L and M06-2X-D3.

### C. Noncovalent Charge-Transfer Dimers

Since the 1990s, it is known that pure and global hybrid functionals severely overestimate binding energies of noncovalent charge-transfer dimers.<sup>65,66</sup> Range-separated functionals achieve qualitative improvement by removing the main cause of the overbinding, which is an unrealistic propensity to transfer electrons between the donor and acceptor. The distinction between range-separated functionals and more traditional DFT approximations is apparent for the interaction energy curve of the  $\text{NH}_3 \dots \text{ClF}$  dimer (Figure 7). The two deepest, most overbinding curves belong to M06-L and B3LYP-D3, a pure functional and a global hybrid, respectively. The range-separated methods, LC-PBETPSS-D3 in particular, yield a



**TABLE I: Mean Absolute Errors (kcal/mol) for the Binding Energies (BE) and Proton-Exchange Barriers (PX) of the CEPX33 Set<sup>a</sup>**

method	BE	PX
LC-PBETPSS-D3	0.28	1.37
LC-PBETPSS	4.71	3.09
M06-L	1.21	1.05
$\omega$ B97XD	0.41	1.80
M06-2X-D3	1.40	6.79
LC- $\omega$ PBE	2.74	3.44
LC- $\omega$ PBE-D3	0.55	5.16
B3LYP-D3	1.99	5.84

<sup>a</sup>Energies are computed with the aug-cc-pVQZ basis.<sup>34</sup> The geometries and reference energies are taken from ref 61.

distinct group of energies close to the reference CCSD(T) curve. The only functional which performs well but is not range-separated, M06-2X-D3, includes a relatively large fraction of the HF exchange (54%).

The LC-PBETPSS-D3 curve is extremely close to the reference curve in the vicinity of the equilibrium separation of  $\text{NH}_3\cdots\text{ClF}$ , but its repulsive part is overestimated. For the compressed dimer at  $R/R_{\text{eq}} = 0.8$ , the interaction energy of LC-PBETPSS-D3 ( $E_{\text{int}} = 2.92$  kcal/mol) is qualitatively different from that of LC- $\omega$ PBE-D3 ( $E_{\text{int}} = -0.72$  kcal/mol), but in accordance with the reference coupled-cluster result ( $E_{\text{int}} = 1.17$  kcal/mol).

Similar behavior of approximate DFT methods is observed for the CT9 set of relatively weakly bound donor-acceptor equilibrium dimers (Table II). The CT9 set gathers the dimers of the CT7/04 set Zhao and Truhlar<sup>67</sup> ( $\text{C}_2\text{H}_2\cdots\text{ClF}$ ,  $\text{C}_2\text{H}_4\cdots\text{F}_2$ ,  $\text{H}_2\text{O}\cdots\text{ClF}$ ,  $\text{HCN}\cdots\text{ClF}$ ,  $\text{NH}_3\cdots\text{Cl}_2$ ,  $\text{NH}_3\cdots\text{F}_2$ ) and a subset of the complexes studied by Yourdkhani et al.<sup>68</sup> ( $\text{CF}_3\text{CN}\cdots\text{BF}_3$ ,  $\text{GeF}_3\text{CN}\cdots\text{BF}_3$ ,  $\text{SiF}_3\text{CN}\cdots\text{BF}_3$ ). The MAEs for CT9 are similar for all range-separated functionals and for M06-2X-D3, but the range-separated hybrids tend to underbind, while M06-2X-D3 predicts excessive binding. Compared with the uncorrected

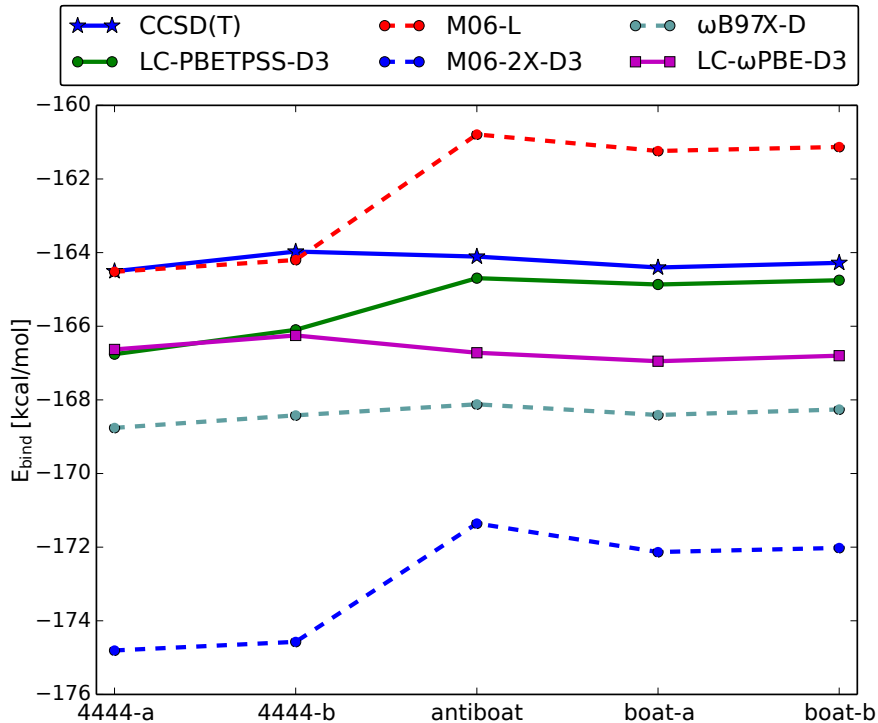


FIG. 6: Binding energies of water 16-mers. The def2-TZVPPD basis<sup>34,45</sup> is employed for LC-PBETPSS-D3. The basis-set extrapolated CCSD(T) energies are taken from ref 63. The energies for the existing DFT methods are taken from ref 64.

variants, both LC-PBETPSS and LC- $\omega$ PBE benefit from the D3 dispersion correction.

For additional comparison, we also employ the low-scaling DLPNO-CCSD(T) wavefunction method. With the MAE of 0.18 kcal/mol on the CT9 set, DLPNO-CCSD(T) is more accurate than any tested DFT method. However, it is still computationally more expensive than single-determinantal DFT approaches owing to the relatively strong dependence on the basis set quality.

#### D. Main-Group Thermochemistry

To test the performance of LC-PBETPSS-D3 for main-group thermochemistry, we use the sets of isodesmic reaction energies,<sup>69</sup> Diels-Alder reaction energies (DARC),<sup>54</sup> and reaction energies with a large contribution of the intramolecular dispersion energy (IDISP).<sup>54</sup>

A general-purpose functional has to describe the energy differences between covalently bound structures while including the contributions from intramolecular noncovalent inter-

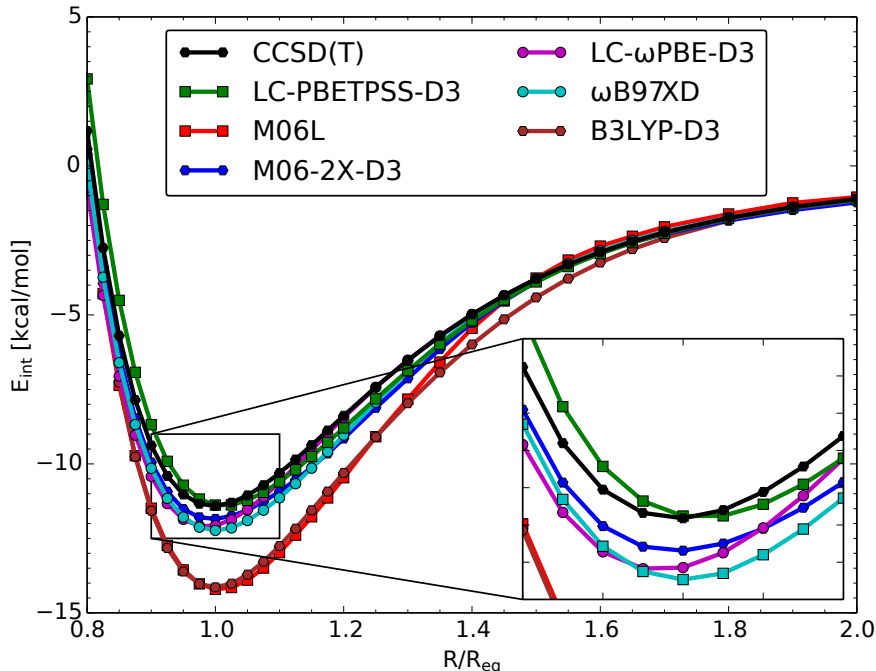
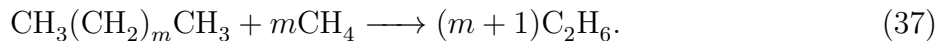


FIG. 7: Interaction energy curves for the  $\text{NH}_3\cdots\text{CIF}$  dimer.

actions. A model case of this kind involves the reaction energies of n-alkane isodesmic fragmentation



Several authors have enumerated the factors which affect the accuracy of approximate DFT for these reactions. Grimme<sup>69</sup> noted that a dispersion correction is crucial, but even a dispersion-corrected semilocal DFT lacks a proper description of middle-range correlation. Johnson et al.<sup>70</sup> ascribed the size-dependent errors in the reaction energies to the deficient description of regions where the reduced density gradient changes upon the reaction. An appropriate description of these regions is provided by the PBEsol exchange energy which obeys the exact second-order expansion for small density gradients.<sup>70,71</sup> Song et al.<sup>72</sup> stressed the importance of correcting the exchange functional via range separation. Finally, Modrzejewski et al.<sup>63</sup> demonstrated a remarkable improvement in the isodesmic reaction energies when using the MCS functional, which combines the range-separated PBEsol exchange and our meta-GGA correlation optimized to work with a dispersion correction.<sup>73</sup>

In our tests, all functionals underestimate alkane stability with the error proportional to the alkane size (Figure 8). The two error curves with the lowest slope belong to LC-PBETPSS-D3 and M06-2X-D3. Without the D3 correction, LC-PBETPSS and LC- $\omega$ PBE

**TABLE II: Mean Absolute Errors (kcal/mol) for the Interaction Energies of the CT9 Set of Charge-Transfer Dimers<sup>a</sup>**

method	MAE
DLPNO-CCSD(T)	0.18
M06-2X-D3	0.37
LC-PBETPSS-D3	0.39
LC-PBETPSS	1.44
LC- $\omega$ PBE-D3	0.41
LC- $\omega$ PBE	1.14
$\omega$ B97XD	0.41
B3LYP-D3	0.73
M06-L	0.81

<sup>a</sup> DFT computations are performed with the def2-QZVPP basis. The reference energies at the CCSD(T) level and the DLPNO-CCSD(T) energies are extrapolated to the basis-set limit (aug-cc-pVTZ  $\rightarrow$  aug-cc-pVQZ) with the automated extrapolation scheme available in ORCA.<sup>60</sup> The same computational procedure is employed for the interaction energy curves of the NH<sub>3</sub>...ClF dimer.

form a group of outliers together with the pure M06-L functional. The dispersion term has only a limited effect on M06-2X, which appears to account for the essential part of the intramolecular dispersion energy via its extensive empirical parametrization.

The DARC subset of the GMTKN30 database<sup>54</sup> comprises fourteen Diels-Alder reaction energies in which the reactants containing multiple conjugated bonds react to form cyclic and bicyclic products (see Figure 1 in ref 74). Most of the existing DFT approximations underestimate the reaction energies in this set.<sup>74</sup> The reasons for that have general impli-

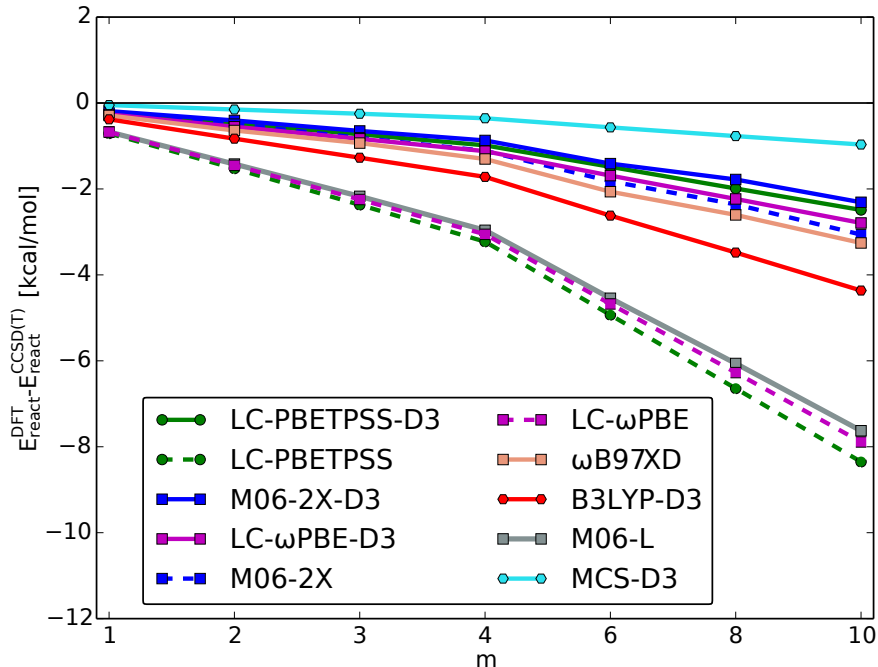


FIG. 8: Errors in isodesmic reaction energies of n-alkane fragmentation. The geometries and reference energies at the CCSD(T) level are taken from ref 69. The def2-QZVP basis is employed for all DFT computations except for MCS-D3. MCS-D3 is a range-separated functional based on the PBEsol exchange.<sup>63</sup> The energies for MCS-D3 are computed using the def2-TZVPP basis.

cations for the application of approximate DFT for main group thermochemistry. Johnson et al.<sup>74</sup> have argued that the reactants of the Diels-Alder reaction have delocalized electron densities, therefore these structures are artificially stabilized due to the self-interaction (delocalization) error. On the products side, the bicyclic molecules have bridgehead carbons whose noncovalent repulsion tends to be overestimated by approximate DFT.<sup>74</sup> Because of these two systematic effects, the energetic gain of going from the reactants to the products is underestimated.

LC-PBETPSS-D3 achieves the lowest mean absolute error of all functionals tested on the DARC set (Table III). The addition of the dispersion correction to LC-PBETPSS reduces the MAE by a factor of four. In contrast, supplying the D3 term to LC- $\omega$ PBE increases the MAE from 6.3 kcal/mol to 10 kcal/mol. The effect of the three-body dispersion term included in LC-PBETPSS-D3+3body is negligible due to the small size of the systems.

The IDISP subset of the GMTKN30 database is composed of six reaction energies in

**TABLE III: Mean Absolute Errors (kcal/mol) for the Reaction Energies of the IDISP and DARC Sets<sup>a</sup>**

method	IDISP	DARC
LC-PBETPSS-D3	2.35 <sup>b</sup>	1.38 <sup>c</sup>
LC-PBETPSS-D3+3body	2.27 <sup>b</sup>	1.37 <sup>c</sup>
LC-PBETPSS	11.38 <sup>b</sup>	6.07 <sup>c</sup>
M06-L <sup>d</sup>	6.55	8.04
M06-2X-D3 <sup>d</sup>	1.71	2.28
LC- $\omega$ PBE-D3 <sup>d</sup>	4.13	10.04
LC- $\omega$ PBE <sup>d</sup>	8.03	6.30
B3LYP-D3 <sup>d</sup>	6.63	10.23
$\omega$ B97XD <sup>d</sup>	2.63	1.98

<sup>a</sup> Reference energies and geometries are obtained from the companion website of ref 54.

<sup>b</sup> Computed with the def2-QZVP basis.

<sup>c</sup> Computed with the def2-QZVPP basis. <sup>d</sup> Ref 54.

which alkanes undergo transformations between structures with different amounts of the intramolecular dispersion energy.<sup>54</sup> A typical reaction included in IDISP is presented in Figure 9. LC-PBETPSS-D3, M06-2X-D3, and  $\omega$ B97XD are the best methods tested on this set (Table III). The D3 correction is important and beneficial for both LC-PBETPSS and LC- $\omega$ PBE. The addition of the three-body D3 term has a noticeable beneficial effect on the reaction energies predicted by LC-PBETPSS-D3+3body.

## E. Excitation Energies

Numerous authors have reported evidence that there exists a marked advantage of using range-separated functionals over more traditional DFT approximations for excitation energies of donor-acceptor systems and for Rydberg transitions, without compromising on valence excitations.<sup>10,13</sup> To test the performance of LC-PBETPSS, we apply it to the lowest charge-

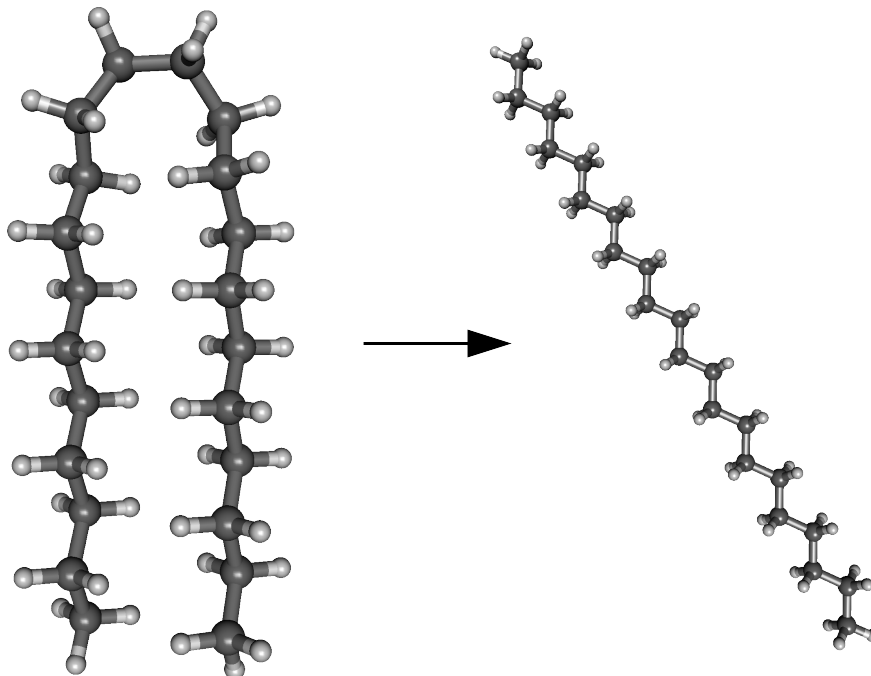


FIG. 9: Example of a reaction included in the test set for intramolecular dispersion interactions (IDISP).<sup>54</sup>

transfer excitations of aromatic donor-tetracyanoethylene (Ar-TCNE) pairs (Table IV) as well as valence and Rydberg excitations of CO, N<sub>2</sub>, H<sub>2</sub>CO, C<sub>2</sub>H<sub>4</sub>, and C<sub>4</sub>H<sub>6</sub> (Table V).

Due to the limitations of the software suite in which LC-PBETPSS has been initially implemented, the excitation energies for this functional are obtained using real-time time-dependent DFT (RT-TDDFT) instead of the usual linear response equations.<sup>75,76</sup> The propagation of the density matrix was carried out for 2500 a.u. (60 fs) for all molecules except for the TCNE-xylene dimer and ethylene, which were propagated for 3000 a.u. and 10 000 a.u., respectively. The time step in each case was  $\Delta t = 0.1$  a.u. (0.0024 fs). Each time a dc pulse with a duration of 0.24 fs and field strength of  $E_{\max} = 0.0001$  a.u. was applied. All RT-TDDFT calculations were carried out in the Molpro program.<sup>52</sup>

LC-PBETPSS achieves about the same level of accuracy for Rydberg, valence, and charge-transfer excitations (Tables IV and V). While the best DFT method for the charge-transfer transitions is  $\omega$ B97X,<sup>17</sup> there is only an insignificant difference between  $\omega$ B97X, LC-PBETPSS, and LC- $\omega$ PBE for valence and Rydberg excitations.

**TABLE IV: Energies (eV) of the Lowest CT Transitions in Gas-Phase Ar-TCNE Complexes<sup>a</sup>**

Ar	benzene	toluene	o-xylene
ref <sup>77</sup>	3.59	3.36	3.15
$\omega$ B97X <sup>17</sup>	3.67	3.34	3.37
LC- $\omega$ PBE	4.00	3.65	3.68
LC-PBETPSS	3.87	3.50	3.49
B3LYP	2.06	1.81	1.88
M06-L	1.65	1.46	1.56
M06-2X	3.03	2.93	2.78
GW <sup>78</sup>	3.58	3.27	2.89
BNL <sup>b</sup>	3.8	3.4	3.0

<sup>a</sup>DFT calculations employ the cc-pVDZ basis set.<sup>34</sup> <sup>b</sup>The range-separated BNL functional<sup>7</sup> includes a system-dependent parameter  $\omega$ . The energies are taken from ref 79.

## F. Symmetry-Adapted Perturbation Theory

Symmetry-adapted perturbation theory provides a framework for computation and interpretation of noncovalent interaction energies.<sup>85</sup> The energy contributions defined in SAPT can be computed using approximate functionals, provided that orbital coefficients, orbital energies, and density response functions are available.

The accuracy of the total interaction energy as well as of the individual SAPT contributions is contingent on the realistic description of the density tail, therefore traditional pure and global hybrid functionals must employ asymptotic corrections of the exchange-correlation potential.<sup>86</sup> Range-separated functionals do not require the corrections which change the decay rate of the potential, but they need a procedure that levels the HOMO energy with negative of the vertical ionization potential (IP).<sup>87</sup> The adjustment of the orbital energy involves tuning of the range-separation parameter for each molecule of interest



**TABLE V: Energies (eV) of Valence and Rydberg Transitions in CO, N<sub>2</sub>, Formaldehyde, Ethylene, and trans-1,3-Butadiene**

	transition	ref	B3LYP	M06-L	M06-2X	$\omega$ B97X <sup>17</sup>	LC- $\omega$ PBE	LC-PBETPSS
CO <sup>a</sup>	$\sigma \rightarrow \pi^*$	8.51 <sup>d</sup>	8.40	8.58	8.22	8.53	8.55	8.66
	$\sigma \rightarrow 3s$	10.78 <sup>d</sup>	9.83	9.35	10.86	10.77	10.84	10.76
	$\sigma \rightarrow 3p\sigma$	11.40 <sup>d</sup>	10.21	9.61	10.86	11.22	11.34	11.15
	$\sigma \rightarrow 3p\pi$	11.53 <sup>d</sup>	10.27	9.87	10.90	11.31	11.42	11.28
N <sub>2</sub> <sup>a</sup>	$\sigma_g \rightarrow 3p\pi_u$	12.90 <sup>d</sup>	11.78	10.85	12.47	12.57	12.68	12.50
	$\sigma_g \rightarrow 3p\sigma_u$	12.98 <sup>d</sup>	11.62	10.53	12.53	12.59	12.70	12.52
	$\pi_u \rightarrow 3s\sigma_g$	13.24 <sup>f</sup>	12.04	11.76	12.49	12.88	13.01	12.86
H <sub>2</sub> CO <sup>a</sup>	$n \rightarrow 3s a_1$	7.09 <sup>d</sup>	6.43	6.14	7.09	7.28	7.26	7.11
	$n \rightarrow 3p b_2$	7.97 <sup>d</sup>	7.15	6.49	7.90	8.12	8.11	7.98
	$n \rightarrow 3p a_1$	8.12 <sup>d</sup>	7.16	6.57	7.78	8.00	8.00	7.84
	$\sigma \rightarrow \pi^*$	8.68 <sup>d</sup>	9.01	7.01	8.81	8.99	9.11	8.92
C <sub>2</sub> H <sub>4</sub> <sup>b</sup>	$\pi \rightarrow 3s$	7.11 <sup>e</sup>	6.56	6.60	6.85	7.38	7.52	7.44
	$\pi \rightarrow \pi^*$	7.96 <sup>c</sup>	7.32	7.18	7.47	7.57	7.63	7.69
	$\pi \rightarrow 3d\delta$	8.90 <sup>e</sup>	7.61	7.22	8.42	8.98	9.23	9.13
	$\pi \rightarrow 3d\delta$	9.08 <sup>e</sup>	7.77	7.47	8.52	9.08	9.33	9.21
	$\pi \rightarrow 3d\pi$	9.33 <sup>e</sup>	7.69	7.52	8.58	9.09	9.38	9.28
	$\pi \rightarrow 3d\pi$	9.51 <sup>e</sup>	8.09	7.92	8.82	9.46	9.79	9.68
C <sub>4</sub> H <sub>6</sub> <sup>b</sup>	$\pi \rightarrow \pi^*$	6.32 <sup>c</sup>	5.54	5.62	5.76	5.88	5.97	5.98
	Ryd (2A <sub>u</sub> )	6.66 <sup>e</sup>	5.88	5.87	6.15	6.84	6.94	6.86
	Ryd (2B <sub>u</sub> )	7.07 <sup>e</sup>	6.36	6.09	6.75	7.29	7.40	7.29
	Ryd (3B <sub>u</sub> )	8.00 <sup>e</sup>	6.74	6.39	7.46	8.04	8.30	8.18
	MAE		0.97	1.36	0.42	0.20	0.23	0.22

<sup>a</sup> Energies are computed with the augmented Sadlej basis.<sup>80</sup>

<sup>b</sup> Energies are computed with the 6-311(3+,3+)G\*\* basis.<sup>81</sup>    <sup>c</sup> Theoretical energy at the FCIQMC level,

ref 82.    <sup>d</sup> Experimental energy, ref 10.    <sup>e</sup> Experimental energy, ref 83.    <sup>f</sup> Experimental energy, ref 84.

to satisfy Koopmans’ theorem:<sup>79</sup>

$$\epsilon_{\text{HOMO}}(\omega) = -\text{IP}(\omega). \tag{38}$$

The procedure of solving Eq. 38 is repeated for each interacting monomer,<sup>87</sup> therefore each monomer is assigned its unique value of  $\omega$ .

To illustrate the importance of using the monomer-dependent range-separation parameters, we employ LC-PBETPSS and the range-separated PBE functional of Henderson et al.<sup>14</sup> (HJS- $\omega$ PBE) to compute the total SAPT interaction energies on the A24 set of noncovalent dimers.<sup>88</sup> Here, the total interaction energy is a sum of the first- and second-order SAPT contributions plus a so-called delta-HF term. Each functional is used to compute the orbital coefficients and energies provided to the SAPT program, but the exchange-correlation kernel is in every case at the adiabatic local density approximation level.

The improvement of LC-PBETPSS upon using Eq. 38 is clear, with over threefold reduction of the MAE for the total interaction energies (Table VI). The errors are reduced by a similar factor for HJS- $\omega$ PBE. With the monomer-dependent parameter  $\omega$ , LC-PBETPSS achieves slightly better accuracy than the common PBE0AC approach, i.e. the PBE0 functional<sup>89</sup> employed with the asymptotic correction of Gruning et al.<sup>86</sup>

**TABLE VI: Mean Absolute Errors (kcal/mol) for the Total SAPT Interaction Energies of the A24 Set<sup>a</sup>**

method	MAE
HJS- $\omega$ PBE( $\omega=0.40$ )	0.19
HJS- $\omega$ PBE( $\omega=*$ ) <sup>b</sup>	0.07
LC-PBETPSS( $\omega=0.35$ )	0.30
LC-PBETPSS( $\omega=*$ ) <sup>b</sup>	0.09
PBE0AC	0.12

<sup>a</sup>SAPT calculations employ the aug-cc-pVTZ basis set. <sup>b</sup>Range-separation parameters are adjusted to satisfy Eq. 38.

## IV. SUMMARY AND CONCLUSIONS

We have proposed a method of creating meta-GGA range-separated exchange functionals from existing semilocal approximations. Owing to the use of the kinetic energy density and the Laplacian, the underlying exchange hole has the exact second-order expansion in the interelectron distance. The importance of this condition is demonstrated for the hydrogenic density, where the functionals derived using the new approach show a clear reduction of the self-interaction errors compared to existing range-separated GGAs.

While the method is general, its performance strongly depends on the selected pair of the base exchange functional and the accompanying correlation. The initial numerical tests on small sets of atomization energies and barrier heights have shown that the preferred pair of the semilocal models is the PBE exchange and the TPSS correlation. Therefore, the only functional considered in the full suite of tests and the method which we recommend for general use is LC-PBETPSS.

The onset of the long-range HF exchange is controlled by the range-separation parameter, which is estimated theoretically and confirmed by empirical optimization to be  $\omega = 0.35$ . For applications in SAPT, we recommend to adjust  $\omega$  to enforce Koopmans’ theorem for the interacting monomers.

Supplementing LC-PBETPSS with the D3 dispersion correction (comprising only the  $1/R^6$  term) generally improves the accuracy of the method for all test sets considered in this work. We observe additional slight improvement when a three-body dispersion term is included for large systems.

As Figure 10 illustrates, the accuracy of LC-PBETPSS-D3 is remarkably consistent across the whole range of tests which probe the performance for noncovalent interaction energies, barrier heights, and thermochemical energy differences. The errors corresponding to LC-PBETPSS-D3 are in most cases either the smallest or close to the best functionals. The only other functional achieving a similar level of consistent accuracy is  $\omega$ B97XD. When applied to excited states of small systems, LC-PBETPSS describes charge-transfer and Rydberg excitations with a similar level of accuracy as valence excitations.

Compared to LC- $\omega$ PBE-D3, the new method offers improved accuracy for the reaction energies of the IDISP set, Diels-Alder reaction energies, and proton-exchange barriers. While LC-PBETPSS-D3 works better for covalent bonds, it does not compromise on the accuracy

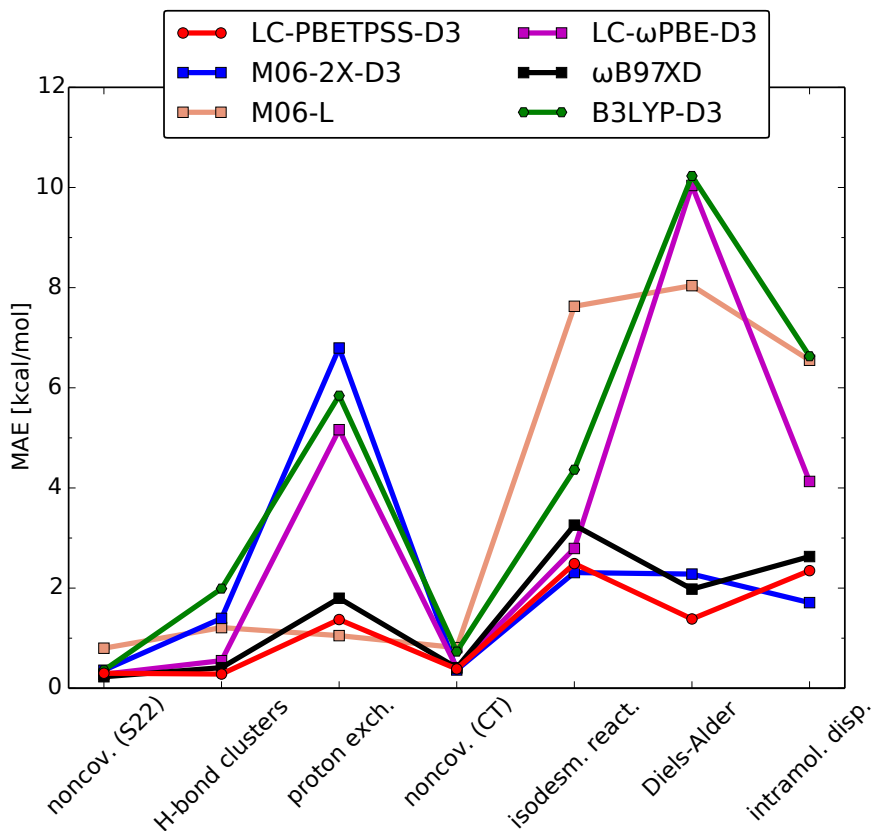


FIG. 10: General view of the performance of DFT methods on the benchmark sets considered in this work. The data points for the isodesmic reaction are the absolute errors for dodecane.

for noncovalent interaction energies. Moreover, the dispersion correction is more compatible with LC-PBETPSS than with LC- $\omega$ PBE. The D3 term is beneficial for LC- $\omega$ PBE when applied to the interaction energies of noncovalent dimers and clusters, but it degrades the accuracy for proton-exchange barriers and Diels-Alder reaction energies. The performance of LC-PBETPSS-D3 is free from such irregularities.

Compared to M06-2X-D3, the new method is more reliable for the binding energies and barrier heights of hydrogen-bonded systems while providing a similar level of accuracy in alkane thermochemistry.

To conclude, the tests presented in this work show that LC-PBETPSS-D3 combines reliability with low empiricism. Further work is needed to assess the performance of the new functional for systems with more complicated electronic structure.

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