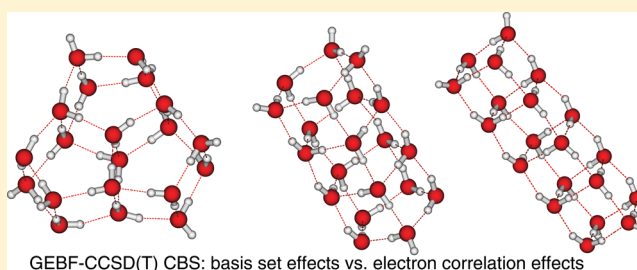


Generalized Energy-Based Fragmentation CCSD(T)-F12a Method and Application to the Relative Energies of Water Clusters (H<sub>2</sub>O)<sub>20</sub>Kedong Wang,<sup>†,‡</sup> Wei Li,<sup>\*,†</sup> and Shuhua Li<sup>†</sup><sup>†</sup>Institute of Theoretical and Computational Chemistry, Key Laboratory of Mesoscopic Chemistry of MOE, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, 210093, People's Republic of China<sup>‡</sup>School of Physics and Electronical Engineering, Henan Normal University, Xinxiang, 453007, People's Republic of China

## Supporting Information

**ABSTRACT:** The generalized energy-based fragmentation (GEBF) approach has been implemented for the explicitly correlated F12a of coupled-cluster with the noniterative triples corrections [CCSD(T)-F12a] method for medium- and large-sized systems. By combining the canonical Hartree–Fock (HF) total energies and the GEBF-X correlation energies, the GEBF-X/HF method is illustrated to be more accurate than the origin GEBF-X method, where X could be any electron correlation method, such as second-order Møller–Plesset perturbation theory (MP2), MP2-F12, CCSD(T), and CCSD(T)-F12a. By combining the GEBF-X/HF results at the MP2-F12 and CCSD(T)-F12a levels, we can approximately achieve the CCSD(T) complete basis set (CBS) limit. Our test calculations for 10 low-energy isomers of water 20-mers show that for the relative energies of large water clusters, both the basis set and high-level electron correlation effects should be taken into account, in which the former is even more important. In addition, the GEBF-CCSD(T)/HF method at the CBS limit is used to evaluate 32 levels of density functional theory (DFT) methods. The results show that the DFT methods are difficult to predict the relative energies between the isomers of water 20-mers. The GEBF-CCSD(T)/HF method at the CBS limit is expected to be a benchmark for DFT and other electron correlation methods for medium- and large-sized systems with complex structures, in which both the basis set and electron correlation effects are important.



## 1. INTRODUCTION

High-level electron correlation methods, such as coupled-cluster (CC) theory, are very difficult for medium- and large-sized systems due to extreme high scaling and very slow convergence to the complete basis set (CBS) limit. By introducing the short-range correlation factors, the explicitly correlated R12 and F12 methods can almost achieve the CBS limit with medium-sized basis sets.<sup>1–3</sup> In order to attack the high scaling of electron correlation methods, two categories of linear scaling algorithms have been implemented, including local correlation approaches<sup>4–22</sup> and fragment-based approaches.<sup>23–51</sup> The main idea of the fragment-based approaches is that the total energy of a large system can be obtained from the energies, density matrices, or other properties of constructed valence saturated subsystems. An energy-based fragmentation (EBF) approach for the ground-state energy and gradients of general systems was proposed by Li and co-workers,<sup>34</sup> and almost at the same time, an analogical method, the systematic molecular fragmentation (SMF) approach, was proposed by Collins and Deev.<sup>39</sup> Subsequently, by constructing subsystems and assembling their energies in different ways, various energy-based approaches were also developed by other groups.<sup>43,45,46,48,49</sup>

In order to treat the general macromolecules or molecular clusters with charge or polar groups, a generalized energy-based

fragmentation (GEBF) approach was developed by Li and co-workers<sup>35</sup> by embedding each subsystem in point charges on those atoms outside of the subsystem. The performance of some other energy-based approaches could also be improved by employing the electrostatically embedding strategy.<sup>32,42,45,51</sup> With an automatic fragmentation procedure,<sup>36</sup> the GEBF approach has been implemented for the calculations of ground-state energy, molecular geometry, and molecular properties at various levels of electron structure methods<sup>35,37,52–57</sup> and been used for the theoretical studies of water clusters, biological molecules, and supramolecules.<sup>58–61</sup> Recently, the GEBF approach has been implemented for the explicitly correlated second-order Møller–Plesset perturbation theory F12 (MP2-F12) method,<sup>62</sup> which can almost achieve the MP2 CBS limit with the aug-cc-pVDZ (aVDZ) basis set for the binding energy in the methanol–water clusters.<sup>38</sup>

The relative energies or binding energies of small- and medium-sized water clusters have been intensively studied by density functional theory (DFT) and *ab initio* methods,<sup>16,27,57,59,63–80</sup> in which the CC singles and doubles (CCSD) with noniterative triples corrections [CCSD(T)] method<sup>81</sup> is usually employed as a benchmark.<sup>68–70,73,77</sup> By

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combining the MP2 [or resolution-of-identity MP2 (RI-MP2)] at the CBS limit and CCSD(T) with medium-sized basis sets, CCSD(T) results at the CBS limit were obtained for water clusters only up to the water decamer.<sup>69,70,77</sup> Recently, the conventional CCSD(T) relative energies of five water 16-mers and two water 17-mers were obtained with the aug-cc-pVTZ (aVTZ) basis set by using a supercomputer.<sup>73</sup> With these CCSD(T) results, the performances of various DFT functionals have been evaluated.<sup>68,70,80</sup> In addition, local correlation methods or fragment-based approaches can be used for CC calculations of large water clusters, but usually with small- or medium-sized basis sets in order to obtain reasonable results with affordable computational costs.<sup>16,27,57,59,71,79</sup> However, the high-level CC calculations at the CBS limit have rarely been reported for large water clusters, in which both the basis set and electron correlation effects are important. Very recently, the CCSD(T)/CBS results for water 26-mers have been well reproduced with the CCSD(T)-F12b:EE-3B approximation.<sup>82</sup>

In the present work, we have implemented the GEBF approach for the explicitly correlated CCSD(T)-F12a method,<sup>83</sup> a fixed amplitude approximation of the exact CCSD(T)-F12 method, in order to approximately achieve the CCSD(T) CBS limit for medium- and large-sized systems. In this implementation, we combine the canonical Hartree–Fock (HF) energy and the GEBF-X correlation energy to obtain the GEBF-X/HF energy, where X could be any electron correlation method, such as MP2, MP2-F12, CCSD, CCSD-F12a, CCSD(T), or CCSD(T)-F12a. The idea of combining HF reference and low scaling correlation energy is also used in the electrostatically embedded many-body correlation energy (EE-MB-CE) method<sup>33,79</sup> and cluster-in-molecule (CIM) method.<sup>14–19</sup> In the EE-MB-CE method, the  $n$ -body terms are generated by full  $n$ -body expansions (or partial expansions with a cutoff), whereas in the GEBF-X/HF method, the  $n$ -fragment terms are derived from primary subsystems, which are constructed by adding environmental fragments to central fragments. The EE-3B-CE method was shown to be able to provide accurate results for the relative energies of water 16-mers at the CCSD(T) level.<sup>79</sup> In the CIM method, the construction of subsystems is similar to that of primary GEBF subsystems. But the CIM subsystems are based on localized molecular orbitals (LMOs), instead of fragments, with no need of extra hydrogen atoms for cut bonds. The total correlation energy is assembled by the contribution of occupied LMOs, which are mathematically taken from the “primitive” subsystems (“derivative” subsystems are not required). Thus, the CIM method is able to be applied to more general systems, including open-shell systems, but could not be simply extended to more electron correlation methods without revising the corresponding program codes. In this work, we combine GEBF-MP2-F12/HF with the aug-cc-pVQZ (aVQZ) basis set and GEBF-CCSD(T)-F12a/HF with aVDZ basis set to approximately achieve the CCSD(T) CBS limit. Our illustrative calculations for the relative energies of 10 water 20-mers show that the GEBF-CCSD(T)/HF method at the CBS limit is able to act as a benchmark for medium- and large-sized systems to evaluate various *ab initio* and DFT methods.

The paper is organized as follows. In section 2, the improved GEBF approach is introduced, and the computational details are described. In section 3, the GEBF-CCSD(T)/HF results at the CBS limit of water 20-mers are illustrated to validate other electron correlation methods and various DFT functionals. Finally, a brief summary is given in section 4.

## 2. METHODOLOGY

In the GEBF method, a target system is divided into many fragments by an automatic procedure.<sup>35,36</sup> For each fragment, denoted as a central fragment, a primitive subsystem is constructed by adding the environmental fragments with a distance threshold  $\zeta$ , followed by eliminating those small primitive subsystems, which are totally incorporated in larger ones. The number of irreducible primitive subsystems is denoted as  $M_p$ . For each primitive subsystems  $k$ , a coefficient  $C_k$  ( $k = 1, \dots, M_p$ ) is defined and set to one. From the primitive subsystems, the derivative subsystems are constructed and the corresponding coefficients  $C_k$  ( $k = M_p + 1, \dots, M$ ) are determined to guarantee that the net number of each  $n$ -fragment ( $n = \lambda - 1, \dots, 1$ ) term be only one, where  $\lambda$  is the maximum number of fragments in the primitive subsystems (including the central fragment) and the net number of an  $n$ -fragment term  $A$  is defined as the summation of coefficients for those subsystems including term  $A$  as a subunit,  $\sum_{k: A \in k} C_k$ . For all subsystems (with the total number being  $M$ ), the unsaturated terminal atoms at the place of the broken single covalent bond are capped with hydrogen atoms. In order to take the long-range electrostatic interaction and polarization effects into account, each subsystem is electrostatically embedded in the field of point charges at the places of all atoms outside this subsystem. The point charges are extracted by a two-step iteration from the central fragments in the primitive subsystems and electrostatically embedded primitive subsystems, respectively. Then, the GEBF total energy of the target system can be directly obtained from the conventional energies of all electrostatically embedded subsystems as follows:<sup>35</sup>

$$E_{\text{Tot}}^{\text{GEBF}} = \sum_k C_k \tilde{E}_k - \left( \sum_k C_k - 1 \right) \sum_A \sum_{B>A} \frac{Q_A Q_B}{R_{AB}} \quad (1)$$

where  $C_k$  and  $\tilde{E}_k$  are the coefficient and the energy (including the self-energy of point charges) of the  $k$ th embedded subsystem, respectively,  $Q_A$  is the charge on atom  $A$ , and  $R_{AB}$  is the distance between two atoms  $A$  and  $B$ .

The GEBF method has been used to compute the ground-state energies, optimized molecular geometries, and molecular properties for a broad range systems at different levels of quantum chemistry methods.<sup>35,38,52–54,56,57</sup> However, for some systems in need of very high accuracy, some higher level methods, such as CCSD(T), with quite large basis sets are usually required. In this work, the CCSD(T)-F12a method<sup>83,84</sup> is employed for the calculations of subsystems in order to achieve more accurate results by using a medium basis set such as aVDZ, as we did in GEBF-MP2-F12 work.<sup>38</sup> In order to predict the small energies difference of water clusters without leading to relative large subsystems, we introduce several strategies to improve the GEBF approach. First, for a target system, we combine the conventional HF energy and GEBF-X correlation energy to obtain a more accurate GEBF-X/HF energy as follows:

$$E_{\text{Tot}}^{\text{GEBF-X/HF}} = E_{\text{Tot}}^{\text{HF}} + E_{\text{Tot}}^{\text{GEBF-X}} - E_{\text{Tot}}^{\text{GEBF-HF}} \quad (2)$$

where X could be any electron correlation method, such as MP2, MP2-F12, CCSD, CCSD(T), CCSD(T)-F12a, etc. Second, the point charges on atoms are obtained by the conventional HF calculation instead of the extraction from the central fragment of primitive subsystems in the original GEBF work. Furthermore, we introduce another parameter  $\lambda_{\text{max}}$  to

avoid those relative large primitive subsystems. For a given central fragment, each environmental fragment within the distance  $\zeta$  is ranked in terms of its distance (from the central fragment). If the number of environmental fragments is larger than  $\lambda_{\max} - 1$ , the first  $\lambda_{\max} - 1$  fragments will be retained to ensure that the total number of fragments within the primitive subsystem does not exceed  $\lambda_{\max}$ . In addition, if the distance between a pair of fragments, which does not emerge in existing subsystems, is less than  $2\zeta$ , an additional electrostatically embedded two-fragment subsystem will be constructed to incorporate more two-body terms.

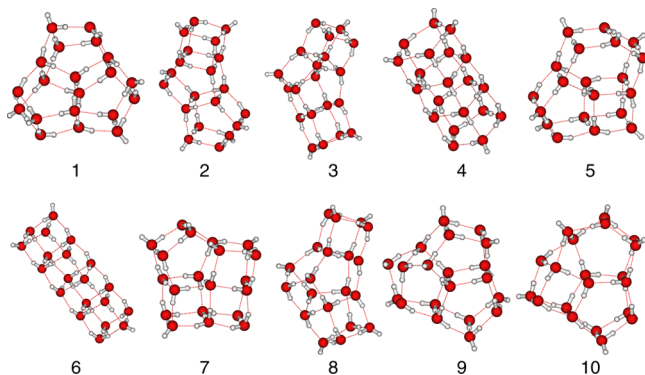
Instead of an extrapolation scheme, a procedure for CCSD(T) CBS limit relative energies was employed for water hexamers by combining MP2-R12 relative energies with a large basis set (considered as MP2 CBS limit) and  $\delta E_{\text{MP2}}^{\text{CCSD(T)}}$  correction.<sup>69</sup> In this work, the GEBF-MP2/HF at the CBS limit relative energies are approximately determined from the GEBF-MP2-F12/HF with the aVQZ basis set (172 basis functions per water molecule). Then, the GEBF-CCSD(T)/HF relative energies at the CBS limit can be obtained as follows:

$$\Delta E_{\text{CBS}}^{\text{GEBF-CCSD(T)/HF}} = \Delta E_{\text{CBS}}^{\text{GEBF-MP2/HF}} + \delta E_{\text{GEBF-MP2-F12}}^{\text{GEBF-CCSD(T)-F12a}} \quad (3)$$

where  $\delta E_{\text{GEBF-MP2-F12}}^{\text{GEBF-CCSD(T)-F12a}}$  is the energy difference between the GEBF-CCSD(T)-F12a/HF and GEBF-MP2-F12/HF relative energies with the aVDZ basis set. The corresponding GEBF-CCSD/HF relative energies at the CBS limit can be assembled in a similar way.

### 3. RESULTS AND DISCUSSION

In this section, the GEBF-X/HF method is illustrated for the relative energies of 10 low-energy isomers of water clusters ( $\text{H}_2\text{O}$ )<sub>20</sub> in Figure 1, and the GEBF-X/HF [X = MP2, CCSD,

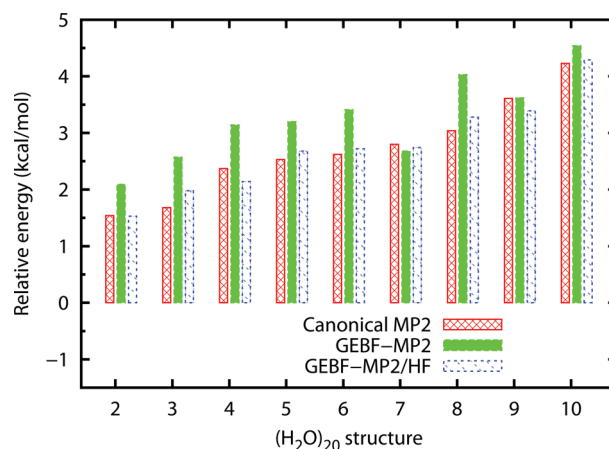


**Figure 1.** The 10 low-energy isomers of water clusters, ( $\text{H}_2\text{O}$ )<sub>20</sub>, obtained by the TIP4P force field and reordered according to the conventional MP2 single point energies with the aug-cc-pVDZ basis set.

and CCSD(T)] results at the CBS limit are determined. The Cartesian coordinates of the 10 isomers, which were determined using the TIP4P force field<sup>85</sup> by Kazimirski and Buch,<sup>86</sup> are presented in the Supporting Information. For all isomers, the conventional MP2 and various DFT calculations are performed for comparison, and the density-fitting (DF) is employed in all of the HF, MP2, and MP2-F12 calculations unless otherwise specified. All of the GEBF calculations are performed with the LSQC program.<sup>87</sup> The conventional HF and MP2 without DF, and some levels of DFT (including

B3LYP,<sup>88,89</sup> BH&HLYP,<sup>90</sup> X3LYP,<sup>91</sup> B3P86,<sup>92</sup> B3PW91,<sup>93</sup> B97-D,<sup>94</sup> B98,<sup>95</sup>  $\omega$ B97X,<sup>96</sup>  $\omega$ B97X-D,<sup>97</sup> M05,<sup>98</sup> M05-2X,<sup>98</sup> M06-2X,<sup>99</sup> M06-L,<sup>100</sup> PBE,<sup>101</sup> LC- $\omega$ PBE,<sup>102</sup> TPSSH,<sup>103</sup> and  $\tau$ HCTC<sup>104</sup>) calculations are carried out with the Gaussian 09 program.<sup>105</sup> The conventional DF-HF, DF-MP2, DF-MP2-F12, CCSD(T), and CCSD(T)-F12a calculations are carried out with the MOLPRO 2012 package.<sup>106,107</sup> The PWB6K,<sup>108</sup> PW6B95,<sup>108</sup> and MPW1B95<sup>109</sup> functionals results are obtained with the Q-Chem 3.2 package.<sup>110</sup> The M08-HX,<sup>111</sup> M08-SO,<sup>111</sup> and M11<sup>112</sup> functionals calculations are performed with the GAMESS package.<sup>113</sup> For B3LYP, BH&HLYP, B3PW91, PBE, LC- $\omega$ PBE, TPSSH, PWB6K, PW6B95, and MPW1B95 functionals, the corresponding results with empirical D3 dispersion corrections are also provided.<sup>114</sup> In the DF-MP2-F12 calculations, the DF is used to compute F12 corrections, which are then added to the DF-MP2 correlation energy.<sup>62,115</sup> In the GEBF calculations, each water molecule is taken as a fragment, and the distance threshold ( $\zeta$ ) is set as 3.0 Å. The maximum number of fragments in subsystems ( $\lambda_{\max}$ ) is set as 5 in order to compromise between the accuracy and efficiency, and the natural population analysis (NPA)<sup>116,117</sup> at the HF level is employed to generate background point charges. With the thresholds, the average number of subsystems for the 10 isomers is 129, and the average numbers of  $n$ -fragment ( $n = 5, 4, 3$ , and  $2$ ) terms included in subsystems of the 10 isomers are 15, 81, 152, and 140, respectively.

In order to validate the accuracy of the improved GEBF approach, we compared in Figure 2 and Table 1 the canonical



**Figure 2.** Comparison of canonical MP2, GEBF-MP2, and GEBF-MP2/HF relative energies of the 10 isomers of water cluster ( $\text{H}_2\text{O}$ )<sub>20</sub> with the aug-cc-pVDZ basis set.

MP2, GEBF-MP2, and GEBF-MP2/HF relative energies of the 10 water 20-mers (with respect to the first one) with the aVDZ basis set. First, it can be seen from Table 1 that the relative energies predicted by the DF-MP2 method are almost identical to those by the MP2 method without density-fitting. From Table 1, we can also see that the maximum unsigned error (MUE) and the nonparallelity error (NPE; defined as the difference between the largest positive and largest negative signed errors) for the GEBF-MP2 results relative to canonical MP2 results are 0.98 and 1.11 kcal/mol, respectively. The GEBF-MP2 relative energies are not accurate enough for predicting the stability orders of the water 20-mers (due to very small relative energies among isomers). For example, from Figure 2, one can see that the GEBF-MP2 method predicts



**Table 1.** Comparison of Canonical MP2, GEBF-MP2, and GEBF-MP2/HF Relative Energies (with Respect to the First Isomer) of the 10 Low-Energy Isomers of Water Clusters ( $\text{H}_2\text{O}$ )<sub>20</sub> with the aVDZ Basis Set<sup>a</sup>

isomer	cano. MP2 <sup>b</sup>	GEBF-MP2	GEBF-MP2/HF
1	0.00 (0.00)	0.00	0.00
2	1.54 (1.55)	2.09	1.53
3	1.68 (1.69)	2.57	1.98
4	2.37 (2.35)	3.14	2.14
5	2.53 (2.52)	3.20	2.68
6	2.62 (2.60)	3.41	2.72
7	2.80 (2.78)	2.68	2.74
8	3.04 (3.04)	4.03	3.28
9	3.61 (3.60)	3.62	3.39
10	4.23 (4.21)	4.54	4.29
MUE <sup>c</sup>	0.00	0.98	0.31
NPE <sup>d</sup>	0.00	1.11	0.54

<sup>a</sup>Density-fitting is employed in the HF and MP2 calculations unless otherwise specified, and all energies are in kcal/mol. <sup>b</sup>The canonical MP2 results without density-fitting are included in parentheses. <sup>c</sup>Maximum unsigned error, relative to the canonical MP2 results, in kcal/mol. <sup>d</sup>Nonparallelity error, relative to the canonical MP2 results, in kcal/mol.

isomer 7 to be more stable than isomer 6, while the canonical MP2 predicts a reverse order. However, with the GEBF-MP2/HF method, the corresponding MUE and NPE are significantly reduced to 0.31 and 0.54 kcal/mol, respectively, and the orders of stabilities for all isomers are correctly reproduced. Table S1 in the Supporting Information shows that the relative energy differences between GEBF-HF and conventional HF with the aVDZ basis set vary from 0.52 to 1.01 kcal/mol for isomers 2–6 and 8, which are uncompact structures, while isomer 1 and the remaining ones are all compact ones (see Figure 1). However, with the aVQZ basis set, the relative energy differences for those uncompact structures are 0.43 at most. It indicates that the errors in the GEBF-HF calculations are mainly attributed to the different amount of basis set superposition errors (BSSEs) between compact and uncompact isomers, which become smaller with a large basis set. Thus, the GEBF-X/HF method is able to reproduce the corresponding canonical X results for water 20-mers.

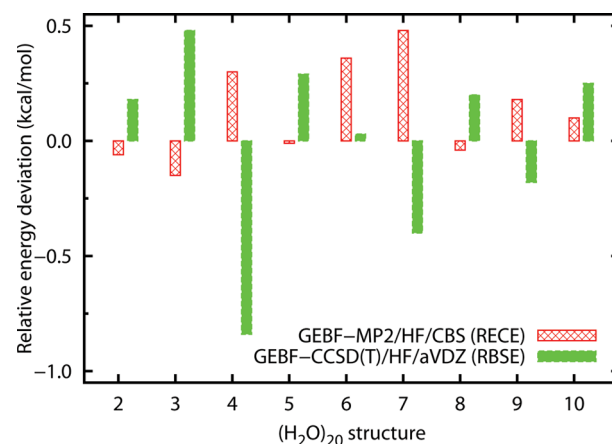
To illustrate the contributions of basis set and electron correlation effects for the relative energies of these water clusters, we compared the GEBF-X/HF [ $X = \text{MP2}$ , CCSD, and CCSD(T)] relative energies with the aVDZ basis set and at the CBS limit of the 10 water 20-mers in Table 2, in which the GEBF-CCSD(T)/HF results at the CBS limit are used as benchmarks to evaluate other results. The corresponding GEBF total energies are provided in Table S2 in the Supporting Information. First, we can see from Table 2 and Figure 1 that the isomers 4, 6, and 7 contain 10, 12, and 9 four- and five-hydrogen-bond-coordinated water molecules, respectively, whereas all the remaining isomers contain eight ones. From Table 2, one can also see that the calculations at the CBS limit show better performance than all of the remaining calculations with the aVDZ basis set. For example, the MUE and NPE for the GEBF-MP2/HF results at the CBS limit are 0.48 and 0.62 kcal/mol, respectively, which are about half of the corresponding values for the GEBF-CCSD(T)/HF results with the aVDZ basis set, 0.84 and 1.31 kcal/mol, respectively. Furthermore, the deviations of the GEBF-MP2/HF relative energies at the CBS

**Table 2.** Comparison of GEBF-X/HF [ $X = \text{MP2}$ , CCSD, and CCSD(T)] Relative Energies (with Respect to the First Isomer) of the 10 Low-Energy Isomers of Water Clusters ( $\text{H}_2\text{O}$ )<sub>20</sub> with the aVDZ Basis Set and at the CBS Limit<sup>a</sup>

isomer	$N_{4,5}$ <sup>b</sup>	GEBF-MP2/HF		GEBF-CCSD/HF		GEBF-CCSD(T)/HF	
		aVDZ	CBS	aVDZ	CBS	aVDZ	CBS
1	8	0.00	0.00	0.00	0.00	0.00	0.00
2	8	1.53	1.30	1.54	1.34	1.54	1.36
3	8	1.98	1.47	1.99	1.50	2.10	1.62
4	10	2.14	2.98	1.96	2.80	1.84	2.68
5	8	2.68	2.36	2.52	2.23	2.66	2.37
6	12	2.72	2.67	2.78	2.72	2.34	2.31
7	9 (1)	2.74	3.18	2.66	3.06	2.30	2.70
8	8	3.28	3.06	3.20	3.00	3.30	3.10
9	8	3.39	3.58	3.32	3.50	3.22	3.40
10	8	4.29	4.04	4.19	3.94	4.19	3.94
MUE <sup>c</sup>		0.54	0.48	0.72	0.41	0.84	0.00
NPE <sup>d</sup>		0.96	0.62	1.19	0.56	1.31	0.00

<sup>a</sup>Density-fitting is employed in the HF, MP2, and MP2-F12 calculations, and all energies are in kcal/mol. <sup>b</sup>The total number of four and five hydrogen-bond coordinated water molecules. The number of five coordinated water molecules is included in parentheses if available. <sup>c</sup>Maximum unsigned error, relative to the GEBF-CCSD(T)/HF results at the CBS limit, in kcal/mol. <sup>d</sup>Nonparallelity error, relative to the GEBF-CCSD(T)/HF results at the CBS limit, in kcal/mol.

limit and the GEBF-CCSD(T)/HF relative energies with the aVDZ basis set relative to the GEBF-CCSD(T)/HF relative energies at the CBS limit are displayed in Figure 3. The two



**Figure 3.** Comparison of the deviations of GEBF-MP2/HF relative energies at the CBS limit and GEBF-CCSD(T)/HF ones with the aVDZ basis set with respect to GEBF-CCSD(T)/HF relative energies at the CBS limit of the 10 isomers of water cluster ( $\text{H}_2\text{O}$ )<sub>20</sub>. The two types of deviations define the relative electron correlation errors (RECEs) and the relative basis set errors (RBSEs), respectively, relative to the first isomer.

types of deviations define the relative electron correlation errors (RECEs) and the relative basis set errors (RBSEs), respectively, relative to the first isomer. From Figure 3, we can see that the RBSEs are larger than the RECEs for most of the isomers. The largest RECE (0.48 kcal/mol) emerges for isomer 7, which contains an extra five hydrogen-bond coordinated water molecules (see Table 2) than isomer 1. On the other hand, the largest RBSE (−0.84 kcal/mol) occurs for isomer 4, which

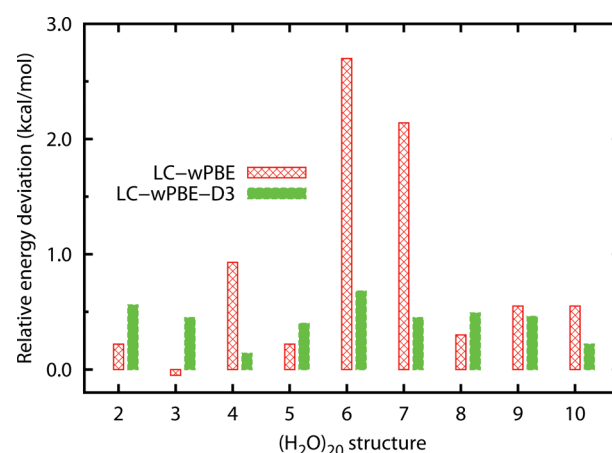
**Table 3.** Comparison of Maximum Unsigned Errors (MUEs) and Nonparallelity Errors (NPEs) of 32 Levels of DFT Relative Energies (with Respect to the First Isomer) Relative to the GEBF-CCSD(T)/HF Results at the CBS Limit of the 10 Low-Energy Isomers of Water Clusters ( $\text{H}_2\text{O}$ )<sub>20</sub><sup>a</sup>

method	MUE <sup>b</sup>	NPE	method	MUE <sup>b</sup>	NPE	method	MUE <sup>b</sup>	NPE
LC- $\omega$ PBE-D3	0.68 (6)	0.68	PWB6K-D3	1.52 (6)	1.52	BH&HLYP	2.81 (6)	2.81
B97-D	0.42 (3)	0.78	PW6B95-D3	1.44 (6)	1.56	M06-L	2.87 (6)	3.05
PBE-D3	0.83 (6)	0.83	M05	1.60 (6)	1.60	PBE	3.13 (6)	3.32
B3LYP-D3	0.79 (9)	0.90	PWB6K	1.75 (6)	1.75	B98	3.34 (6)	3.34
MPW1B95-D3	0.94 (6)	1.03	MPW1B95	2.06 (6)	2.22	X3LYP	3.35 (6)	3.35
B3PW91-D3	0.62 (6)	1.13	PW6B95	2.18 (6)	2.24	B3LYP	3.62 (6)	3.73
BH&HLYP-D3	0.83 (9)	1.13	M08-HX	1.97 (6)	2.55	M06-2X	3.30 (6)	3.81
$\omega$ B97X-D	0.69 (9)	1.17	M11	2.14 (6)	2.68	B3PW91	3.77 (6)	4.22
$\omega$ B97X	0.82 (9)	1.23	LC- $\omega$ PBE	2.70 (6)	2.74	TPSSH	4.40 (6)	4.57
M05-2X	0.66 (6)	1.30	B3P86	2.41 (6)	2.76	$\tau$ HCTC	6.74 (6)	6.75
TPSSH-D3	1.37 (6)	1.37	M08-SO	2.06 (6)	2.81			

<sup>a</sup>The 6-311++G(d,p) basis set is employed in all DFT calculations. All energies are in kcal/mol. <sup>b</sup>The number included in parentheses represents the isomer corresponding to the maximum unsigned error.

contains 10 four-coordinated water molecules. Thus, a different number of four- (and more) hydrogen-bond-coordinated water molecules could lead to a large RECE and even larger RBSE for the relative energies of water clusters. In order to obtain accurate results for medium- and large-sized water clusters, which usually contain a lot of four- (and more) coordinated water molecules, we need to take both the basis set and high-level electron correlation effects into account, in which the former is even more important for systems under study. The GEBF-CCSD(T)/HF method at the CBS limit is expected to provide approximate CCSD(T) results at the CBS limit for those water clusters.

Finally, the GEBF-CCSD(T)/HF results at the CBS limit are employed as benchmarks to evaluate 32 levels of DFT functionals, as described in the previous context, with the Pople's 6-311++G(d,p) basis set, which is popular in DFT studies to obtain reasonable results. The MUEs and NPEs of all of the DFT results are listed in Table 3, and all of the relative energies are included in Table S3 in the Supporting Information. From Table 3, we can find that without the empirical dispersion corrections, the  $\omega$ B97X and M05-2X functionals show relatively satisfactory performance with the NPEs being 1.23 and 1.30 kcal/mol, respectively. If the empirical dispersion corrections are taken into account, the results are noticeably improved, in which the LC- $\omega$ PBE-D3 and B97-D are the best two functionals, with NPEs being only 0.68 and 0.78 kcal/mol, respectively. The good performance of  $\omega$ B97X and LC- $\omega$ PBE-D3 has also been shown in the recent DFT studies of water 16-mers.<sup>80</sup> In Figure 4, we compare the relative energy deviations of LC- $\omega$ PBE and LC- $\omega$ PBE-D3 results relative to the GEBF-CCSD(T)/HF results at the CBS limit. From Figure 4 and Table 3, one can see that, (1) with the LC- $\omega$ PBE method, the three largest relative energy deviations are about 0.9–2.7 kcal/mol for isomers 6, 7, and 4, each of which contains more four- and five-coordinated water molecules than the other isomers; (2) even the LC- $\omega$ PBE-D3 method leads to a large deviation as 0.68 kcal/mol (for isomer 6) and thus cannot predict the correct orders of relative stability. Furthermore, from Table 3, we can see that the largest relative energy deviations for most functionals emerge for isomer 6 with the maximum number (12) of four-coordinated water molecules. Thus, even with the empirical dispersion corrections, popular DFT functionals cannot provide uniformly accurate predictions on the relative stability of medium- and



**Figure 4.** Comparison of LC- $\omega$ PBE and LC- $\omega$ PBE-D3 relative energy deviations with respect to GEBF-CCSD(T)/HF relative energies at the CBS limit of the 10 isomers of water cluster ( $\text{H}_2\text{O}$ )<sub>20</sub>. The LC- $\omega$ PBE and LC- $\omega$ PBE-D3 results are obtained with the 6-311++G(d,p) basis set.

large-sized water clusters due to more complicated structures. In addition, from the NPE(DFT) in Table S3, which is defined as the NPE of relative energies from different DFT functionals for each isomer, we find the three largest NPE(DFT) values (10.94, 5.39, and 3.77 kcal/mol) occur also for the isomers 6, 7, and 4, respectively. It indicates that the different DFT functionals could give a broad range of relative energies for isomers with a very different number of four- (and more) coordinated water molecules. Then, the GEBF-CCSD(T)/HF method at the CBS limit could be used as an alternative benchmark to validate those DFT functionals.

#### 4. CONCLUSIONS

In this work, the GEBF method has been implemented for the explicitly correlated CCSD(T)-F12a method. The GEBF-X/HF energy (X may be any electron correlation method), which combines the canonical HF energy and the GEBF-X correlation energy, is demonstrated to be more accurate than the original GEBF-X energy for the relative energies of water 20-mers. With a similar strategy, the good performance has also been shown in the EE-3B-CE method by comparing with the EE-3B method for the relative energies of water 16-mers.<sup>79</sup> By combining the GEBF-MP2-F12/HF results with the aVQZ basis set and the

GEBF-CCSD(T)-F12a/HF results with the aVDZ basis set, we can approximately obtain the CCSD(T) results at the CBS limit.

With the present GEBF-X/HF methods, we have investigated the relative energies of 10 low-energy isomers of water 20-mers. Our results show that the GEBF-MP2/HF method can reproduce the canonical MP2 relative energies within about 0.3 kcal/mol. From the GEBF-CCSD(T)/HF results at the CBS limit, we find that for the relative energies of large water clusters, we should take both the basis set and high-level electron correlation effects into account, in which the former is even more important. The GEBF-CCSD(T)/HF results with the aVDZ basis set are no more accurate than the GEBF-MP2-F12/HF ones with aVQZ basis set, which can be approximately considered as MP2 results at the CBS limit.

Furthermore, with the GEBF-CCSD(T)/HF method at the CBS limit, we have evaluated 32 levels of DFT methods for the relative energies of the water 20-mers. The results indicate that without the empirical dispersion corrections, the  $\omega$ B97X and M05-2X functionals can provide relatively satisfactory descriptions, and with the empirical dispersion corrections, the LC- $\omega$ PBE-D3 and B97-D functionals are the two most accurate ones. However, even the LC- $\omega$ PBE-D3 cannot predict the correct relative order of stabilities. Thus, the GEBF-CCSD(T)/HF method at the CBS limit is expected to provide benchmark calculations to validate DFT and electron correlation methods for medium- and large-sized systems, in which both basis set and electron correlation effects are important due to the structural complexity.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

A comparison of GEBF and conventional HF relative energies, the GEBF-X/HF [ $X = \text{MP2}$ , CCSD, and CCSD(T)] total energies with the aVDZ basis set and at the CBS limit, the relative energies of 32 levels of DFT methods, and the Cartesian coordinates of 10 isomers of water 20-mers. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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### Notes

The authors declare no competing financial interest.

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