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REGULAR ARTICLE

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The basis set superposition error in multilevel methods: a test on the H_2O and HF dimer

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Abstract The basis set superposition error (BSSE) is often very important in the accurate calculation of dimerization energies. Accurate prediction of thermochemical properties requires appropriate consideration of the basis set incompleteness error. Multilevel methods introduce adjustable parameters to reproduce experimental data, that is, the higher level correction (HLC) in G3 and adjustable coefficients in the MCCM. However, the HLC term is cancelled out and the adjustable coefficients in the MCCM do not remove the BSSE completely. We have calculated the BSSE involved in the multilevel methods. The H_2O and HF dimer systems were used as a test case. This study shows that empirical coefficients do reduce the BSSE in some cases and an MCCM with good parameters can be used to reproduce dimerization energies within chemical accuracy without the BSSE correction.

1 Introduction

In principle, it is known how to calculate the thermochemical properties of molecules to a very high accuracy using quantum chemical calculations. This can be achieved by using very high levels of correlation methods, such as coupled cluster [CCSD(T)] or quadratic configuration [QCISD(T)] methods, and very large basis sets containing high angular momentum functions. The results of these calculations can be extrapolated to the complete basis set limit. However, it is still almost impractical to make reasonably accurate quantitative predictions (with no more than 0.5 kcal/mol of error) based on ab initio calculations except for small systems [1,2]. The computational resources for such calculations are beyond the scope of available technology. An alternative approach applicable for larger molecules is to use a series of high level correlation calculations [e.g., QCISD(T), MP4, CCSD(T)] with moderate-sized basis sets to approximate the result of a more expensive calculation. The Gaussian-*n* series use this idea to predict thermochemical data [1,3–9]. In G2 theory, the basis set truncation error (BSTE), which is a consequence of the incompleteness of the one-electron basis set, is estimated using corrections, which refer to the MP2/6-311+(3df,2p) level of theory, and the remaining correlation effect and the basis-set deficiency are corrected by adding the higher level correction (HLC). Another approach for computing thermochemical data that has been proposed is a scaling of the calculated energy using multiple parameters determined by fitting to experimental data. Recently, Truhlar et al. have suggested more elaborate schemes that combine scaling, extrapolation to infinite basis set, and fitting to a set of experimental data [10–16]. In these methods, the total energy is written as a linear combination of energy terms with different basis sets, and coefficients are adjusted to fit experimental data (atomization energies). The BSTE correction can be included in some of the coefficients. These linear combination methods were called multicoefficient-correlated quantum mechanical methods (MCCM).

Although the BSTE has been considered to compute accurate thermochemical properties of most molecules, the basis set superposition error (BSSE) has not been removed completely in the interaction energies. Most of the calculations for the molecular complexes take the supermolecular approach, where the interaction energy of the complex is obtained as the energy difference between the complex and the monomers. In the Gaussian-*n* series calculations, the HLC term is cancelled out in the interaction energy, and the G2 and G3 methods approximate the interaction energies at the QCISD(T) level with the 6-311+(3df,2p) and the *G3large* basis sets, respectively. Therefore, the BSSE is inevitably included in the interaction energy from the Gaussian-*n* series calculations, although it is considered to be small. No systematic studies have been undertaken yet. In the MCCM, final energy of a molecule is represented by the linear combination of energy terms with empirical coefficients. BSSEs are present not only in non-bonded interactions, but also in covalent

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interactions. The MCCM was developed for covalent interactions without turning on the counterpoise corrections to the BSSE, so one might think that the incompleteness of the basis sets was absorbed into the empirical parameters. However, although the empirical parameters in MCCM can correct the incompleteness of the basis sets present in covalent interactions, it does not assure the correction of BSSE in the dimerization energy. Note that although the HLC was introduced to correct higher level correlation energies and the incompleteness of the basis sets in the Gaussian-*n* methods, this is cancelled out in computing dimerization energies, which may generate large BSSE. The same thing may happen here. More specifically, the basis set incompleteness error (BSIE) in the atomization energies of two monomers corrected by empirical parameters might be partly concealed out by that of the dimer. The BSIEs are not the same for monomer and dimer, but each MCCM uses the same set of coefficients regardless of molecular species, so the BSSE in the dimerization energy cannot be removed completely. Therefore, if one wants to predict dimerization energies accurately, it should be considered properly even with the MCCM. It is also possible that the size of the BSSE depends on the adjusted coefficients.

Although the BSSE of the Gaussian-*n* series and MCCM methods may be quite small since they are developed to predict thermochemical data very accurately (with no more than 1 kcal/mol of error), it is still important in order to predict the small interaction energy of van der Waals complex accurately. This study will show how important and large the BSSE is in the multilevel methods. A conceptually simple way of accounting for BSSE is the counterpoise (CP) correction method, in which the energies of the fragments are calculated in the full basis of the complex, and these CP-corrected energies are used for the energies of the fragments when computing the interaction energy.

The hydrogen fluoride dimer $(HF)_2$ and the water dimer $(H_2O)_2$ have been the subject of numerous experimental and theoretical studies. Hobza et al. [17] have found that the equilibrium geometry of the water dimer from the CP-corrected potential energy surface (PES) differs from the one determined from the standard PES and the difference becomes small only with the largest basis set. The convergence of geometrical data at the CP-corrected PES is very slow and reliable values are obtained only for very large basis sets, which are not applicable for larger clusters. Xantheas [18] has pointed out that the omission of the fragment relaxation energy terms from the estimation of the BSSE corrections can introduce significant errors when the total fragment relaxation energy is either larger or comparable with the correction due to the incompleteness of the basis set and alter the convergence pattern of the interaction energy toward the CBS limit. Many theoretical studies have concentrated on determining a potential energy function that could be used to model and interpret experimental data for HF dimer [19,20]. The use of a high level of theory is necessary to treat the electron correlation for the structure, energies, and harmonic frequencies of $(HF)_2$ properly [21–23]. Recently, Peterson and Dunning [24] reported the geometry, equilibrium dissociation energy and total energy of $(HF)_2$ at the CCSD(T) level with a large correlation consistent basis set as the highest level of theory.

In this study we have focused on the interaction energies and the BSSE including the fragment relaxation energy depending on multilevel methods. We have used the hydrogen fluoride dimer $(HF)_2$ and the water dimer $(H_2O)_2$ as a test.

2 Computational methods

The BSSE was corrected by the Boys and Bernardi [25,26] counterpoise correction scheme,

$$E_\mathrm{BSSE} = [E_\mathrm{m}(M_1) - E_\mathrm{d}(M_1')] + [E_\mathrm{m}(M_2) - E_d(M_2')] + E_\mathrm{rel} \tag{1}$$

$$E_\mathrm{rel} = [E_\mathrm{m}(M_1') - E_\mathrm{m}(M_1)] + [E_\mathrm{m}(M_2') - E_\mathrm{m}(M_2)] \tag{2}$$

where $E_\mathrm{m}(M)$ and $E_\mathrm{d}(M')$ are the energies of the monomer in its own basis set and in the basis set of the hydrogen-bonded dimer, respectively, and M and M' denote the optimized geometry of monomer and the geometry of the monomer in the optimized dimer, respectively. The fragment relaxation energy (E_rel), that is, the energy associated with the transition from the optimized geometry of monomer to the geometry, which the monomer has in the dimer should be also included in the correction of the BSSE. The corrected dimerization energy is determined as follows:

$$\begin{aligned} E_\mathrm{corr} &= E_\mathrm{d}(D) - [E_\mathrm{m}(M_1) + E_\mathrm{m}(M_2)] + E_\mathrm{BSSE} \\ &= E_\mathrm{d}(D) - [E_\mathrm{d}(M_1') + E_\mathrm{d}(M_2')] + E_\mathrm{rel} \end{aligned} \tag{3}$$

where $E_\mathrm{d}(D)$ is the energy of the hydrogen-bonded dimer in its own basis set.

The G3 energies for the dimer and monomer can be expressed as

$$\begin{aligned} E_\mathrm{d}^\mathrm{G3}(D) = {} & E_\mathrm{d}[\mathrm{MP4/Dd}](D) \\ & +\{E_\mathrm{d}[\mathrm{MP4/D+d}](D) - E_\mathrm{d}[\mathrm{MP4/Dd}](D)\} \\ & +\{E_\mathrm{d}[\mathrm{MP4/D2dfp}](D) - E_\mathrm{d}[\mathrm{MP4/Dd}](D)\} \\ & +\{E_\mathrm{d}[\mathrm{QCISD(T)/Dd}](D) - E_\mathrm{d}[\mathrm{MP4/Dd}](D)\} \\ & +\{E_\mathrm{d}[\mathrm{MP2(full)/G3Large}](D) \\ & -E_\mathrm{d}[\mathrm{MP2/D2dfp}](D) \\ & -E_\mathrm{d}[\mathrm{MP2/D+d}](D) \\ & +E_\mathrm{d}[\mathrm{MP2/Dd}](D)\} + \mathrm{HLC} \end{aligned} \tag{4}$$

and

$$\begin{aligned} E_\mathrm{m}^\mathrm{G3}(M) = {} & E_\mathrm{m}[\mathrm{MP4/Dd}](M) \\ & +\{E_\mathrm{m}[\mathrm{MP4/D+d}](M) - E_\mathrm{d}[\mathrm{MP4/Dd}](M)\} \\ & +\{E_\mathrm{m}[\mathrm{MP4/D2dfp}](M) - E_\mathrm{m}[\mathrm{MP4/Dd}](M)\} \\ & +\{E_\mathrm{m}[\mathrm{QCISD(T)/Dd}](M) \\ & -E_\mathrm{m}[\mathrm{MP4/Dd}](M)\} \\ & +\{E_\mathrm{m}[\mathrm{MP2(full)/G3Large}](M) \\ & -E_\mathrm{m}[\mathrm{MP2/D2dfp}](M) \\ & -E_\mathrm{m}[\mathrm{MP2/D+d}](M) \\ & +E_\mathrm{m}[\mathrm{MP2/Dd}](M)\} + \mathrm{HLC}, \end{aligned} \tag{5}$$

where the basis sets 6-31G(d), 6-31+G(d), and 6-31G(2df,p) are denoted as Dd, D+d, and D2dfp, respectively. The CP-corrected dimerization energy at the G3 level is given by

$$\begin{aligned}
E_{\mathrm{corr}}^{\mathrm{G3}} &= E_{\mathrm{d}}^{\mathrm{G3}}(D) - 2E_{\mathrm{m}}^{\mathrm{G3}}(M) + E_{\mathrm{BSSE}}^{\mathrm{G3}} \qquad (6)\\
&= \{E_{\mathrm{d}}[\mathrm{MP4/Dd}](D) - 2E_{\mathrm{m}}[\mathrm{MP4/Dd}](M)\\
&\quad +E_{\mathrm{BSSE}}[\mathrm{MP4/Dd}]\}\\
&\quad +\{E_{\mathrm{d}}[\mathrm{MP4/D+d}](D) - 2E_{\mathrm{m}}[\mathrm{MP4/D+d}](M)\\
&\quad +E_{\mathrm{BSSE}}[\mathrm{MP4/D+d}]\}\\
&\quad -\{E_{\mathrm{d}}[\mathrm{MP4/Dd}](D) - 2E_{\mathrm{m}}[\mathrm{MP4/Dd}](M)\\
&\quad +E_{\mathrm{BSSE}}[\mathrm{MP4/Dd}]\}\\
&\quad +\{E_{\mathrm{d}}[\mathrm{MP4/D2dfp}](D) - 2E_{\mathrm{m}}[\mathrm{MP4/D2dfp}](M)\\
&\quad +E_{\mathrm{BSSE}}[\mathrm{MP4/D2dfp}]\}\\
&\quad -\{E_{\mathrm{d}}[\mathrm{MP4/Dd}](D)\\
&\quad -2E_{\mathrm{m}}[\mathrm{MP4/Dd}](M)\\
&\quad +E_{\mathrm{BSSE}}[\mathrm{MP4/Dd}]\}\\
&\quad +\{E_{\mathrm{d}}[\mathrm{QCISD(T)/Dd}](D)\\
&\quad -2E_{\mathrm{m}}[\mathrm{QCISD(T)/Dd}](M)\\
&\quad +E_{\mathrm{BSSE}}[\mathrm{QCISD(T)/Dd}\}\\
&\quad -\{E_{\mathrm{d}}[\mathrm{MP4/Dd}](D) - 2E_{\mathrm{m}}[\mathrm{MP4/Dd}](M)\\
&\quad +E_{\mathrm{BSSE}}[\mathrm{MP4/Dd}]\}\\
&\quad +\{E_{\mathrm{d}}[\mathrm{MP2(full)/G3Large}](D)\\
&\quad -2E_{\mathrm{m}}[\mathrm{MP2(full)/G3Large}](M)\\
&\quad +E_{\mathrm{BSSE}}[\mathrm{MP2(full)/G3Large}]\}\\
&\quad -\{E_{\mathrm{d}}[\mathrm{MP2/D2dfp}](D) - 2E_{\mathrm{m}}[\mathrm{MP2/D2dfp}](M)\\
&\quad +E_{\mathrm{BSSE}}[\mathrm{MP2/D2dfp}]\}\\
&\quad -\{E_{\mathrm{d}}[\mathrm{MP2/D+d}](D) - 2E_{\mathrm{m}}[\mathrm{MP2/D+d}](M)\\
&\quad +E_{\mathrm{BSSE}}[\mathrm{MP2/D+d}]\}\\
&\quad +E_{\mathrm{d}}[\mathrm{MP2/Dd}](D) - 2E_{\mathrm{m}}[\mathrm{MP2/Dd}](M)\\
&\quad +E_{\mathrm{BSSE}}[\mathrm{MP2/Dd}]\}, \qquad (7)
\end{aligned}$$

where the E_{BSSE}[MP4/Dd], for example, is expressed by

$$\begin{aligned}
E_{\mathrm{BSSE}}[\mathrm{MP4/Dd}] = \{&E_{\mathrm{m}}[\mathrm{MP4/Dd}](M_1)\\
&-E_{\mathrm{d}}[\mathrm{MP4/Dd}](M_1')\}\\
&+\{E_{\mathrm{m}}[\mathrm{MP4/Dd}](M_2)\\
&-E_{\mathrm{d}}[\mathrm{MP4/Dd}](M_2')\}\\
&+\{E_{\mathrm{m}}[\mathrm{MP4/Dd}](M_1')\\
&-E_{\mathrm{m}}[\mathrm{MP4/Dd}](M_1)\}\\
&+\{E_{\mathrm{m}}[\mathrm{MP4/Dd}](M_2')\\
&-E_{\mathrm{m}}[\mathrm{MP4/Dd}](M_2)\}, \qquad (8)
\end{aligned}$$

and so forth. So the sum of the BSSE would be

$$\begin{aligned}
E_{\mathrm{BSSE}}^{\mathrm{G3}} = {}& E_{\mathrm{BSSE}}[\mathrm{MP4/Dd}]\\
&+E_{\mathrm{BSSE}}[\mathrm{MP4/D+d}] - E_{\mathrm{BSSE}}[\mathrm{MP4/Dd}]\\
&+E_{\mathrm{BSSE}}[\mathrm{MP4/D2dfp}] - E_{\mathrm{BSSE}}[\mathrm{MP4/Dd}]\\
&+E_{\mathrm{BSSE}}[\mathrm{QCISD(T)/Dd}] - E_{\mathrm{BSSE}}[\mathrm{MP4/Dd}]\\
&+E_{\mathrm{BSSE}}[\mathrm{MP2(full)/G3Large}]\\
&-E_{\mathrm{BSSE}}[\mathrm{MP2/D2dfp}]\\
&-E_{\mathrm{BSSE}}[\mathrm{MP2/D+d}] + E_{\mathrm{BSSE}}[\mathrm{MP2/Dd}]. \qquad (9)
\end{aligned}$$

We can obtain the fragment relaxation energy E_{rel} in the same way.

All of the MCCMs have been described elsewhere in detail [10,12–14,27]. We will use one MCCM method, MCCM-UT-CCSD, to show how to obtain the BSSE. The BSSEs of the MCG3 method can be obtained in the same way as described. The MCCM-UT-CCSD method is written

$$\begin{aligned}
E^{\mathrm{MCCM}} = {}& \mathrm{c1}E[\mathrm{HF/pDZ}]\\
&+\mathrm{c2}\{E[\mathrm{HF/pTZ}] - E[\mathrm{HF/pDZ}]\}\\
&+\mathrm{c3}\{E[\mathrm{MP2/pDZ}] - E[\mathrm{HF/pDZ}]\}\\
&+\mathrm{c4}\{E[\mathrm{MP2/pTZ}] - E[\mathrm{HF/pTZ}]\\
&-E[\mathrm{MP2/pDZ}] + E[\mathrm{HF/pDZ}]\}\\
&+\mathrm{c5}\{E[\mathrm{CCSD/pDZ}] - E[\mathrm{MP2/pDZ}]\}\\
&+E_{\mathrm{so}} + E_{\mathrm{cc}}, \qquad (10)
\end{aligned}$$

where pDZ and pTZ are the cc-pVDZ and cc-pVTZ basis sets, respectively. The CP-corrected dimerization energy is written as

$$\begin{aligned}
E_{\mathrm{corr}}^{\mathrm{MCCM}} &= E_{\mathrm{d}}^{\mathrm{MCCM}}(D) - 2E_{\mathrm{m}}^{\mathrm{MCCM}}(M) + E_{\mathrm{BSSE}}^{\mathrm{MCCM}}\\
&= \{\mathrm{c1}E_{\mathrm{d}}[\mathrm{HF/pDZ}](D) - 2\mathrm{c1}E_{\mathrm{m}}[\mathrm{HF/pDZ}](M)\\
&\quad +\mathrm{c1}E_{\mathrm{BSSE}}[\mathrm{HF/pDZ}]\}\\
&\quad +\{\mathrm{c2}E_{\mathrm{d}}[\mathrm{HF/pTZ}](D) - 2\mathrm{c2}E_{\mathrm{m}}[\mathrm{HF/pTZ}](M)\\
&\quad +\mathrm{c2}E_{\mathrm{BSSE}}[\mathrm{HF/pTZ}]\}\\
&\quad -\{\mathrm{c2}E_{\mathrm{d}}[\mathrm{HF/pDZ}](D) - 2\mathrm{c2}E_{\mathrm{m}}[\mathrm{HF/pDZ}](M)\\
&\quad +\mathrm{c2}E_{\mathrm{BSSE}}[\mathrm{HF/pDZ}]\}\\
&\quad +\{\mathrm{c3}E_{\mathrm{d}}[\mathrm{MP2/pDZ}](D)\\
&\quad -2\mathrm{c3}E_{\mathrm{m}}[\mathrm{MP2/pDZ}](M)\\
&\quad +\mathrm{c3}E_{\mathrm{BSSE}}[\mathrm{MP2/pDZ}]\}\\
&\quad -\{\mathrm{c3}E_{\mathrm{d}}[\mathrm{HF/pDZ}](D) - 2\mathrm{c3}E_{\mathrm{m}}[\mathrm{HF/pDZ}](M)\\
&\quad +\mathrm{c3}E_{\mathrm{BSSE}}[\mathrm{HF/pDZ}]\}\\
&\quad +\{\mathrm{c4}E_{\mathrm{d}}[\mathrm{MP2/pTZ}](D) - 2\mathrm{c4}E_{\mathrm{m}}[\mathrm{MP2/pTZ}](M)\\
&\quad +\mathrm{c4}E_{\mathrm{BSSE}}[\mathrm{MP2/pTZ}]\}\\
&\quad -\{\mathrm{c4}E_{\mathrm{d}}[\mathrm{HF/pTZ}](D) - 2\mathrm{c4}E_{\mathrm{m}}[\mathrm{HF/pTZ}](M)\\
&\quad +\mathrm{c4}E_{\mathrm{BSSE}}[\mathrm{HF/pTZ}]\}\\
&\quad -\{\mathrm{c4}E_{\mathrm{d}}[\mathrm{MP2/pDZ}](D) - 2\mathrm{c4}E_{\mathrm{m}}[\mathrm{MP2/pDZ}](M)\\
&\quad +\mathrm{c4}E_{\mathrm{BSSE}}[\mathrm{MP2/pDZ}]\}\\
&\quad +\{\mathrm{c4}E_{\mathrm{d}}[\mathrm{HF/pDZ}](D) - 2\mathrm{c4}E_{\mathrm{m}}[\mathrm{HF/pDZ}](M)\\
&\quad +\mathrm{c4}E_{\mathrm{BSSE}}[\mathrm{HF/pDZ}]\}\\
&\quad +\{\mathrm{c5}E_{\mathrm{d}}[\mathrm{CCSD/pDZ}](D)\\
&\quad -2\mathrm{c5}E_{\mathrm{m}}[\mathrm{CCSD/pDZ}](M)\\
&\quad +\mathrm{c5}E_{\mathrm{BSSE}}[\mathrm{CCSD/pDZ}]\}\\
&\quad -\{\mathrm{c5}E_{\mathrm{d}}[\mathrm{MP2/pDZ}](D)\\
&\quad -2\mathrm{c5}E_{\mathrm{m}}[\mathrm{MP2/pDZ}](M)\\
&\quad +\mathrm{c5}E_{\mathrm{BSSE}}[\mathrm{MP2/pDZ}]\}. \qquad (11)
\end{aligned}$$

Then the sum of BSSE is given

$$\begin{aligned}E_{\mathrm{BSSE}}^{\mathrm{MCCM}} &= \mathrm{c}1E_{\mathrm{BSSE}}[\mathrm{HF/pDZ}]\\ &\quad +\mathrm{c}2E_{\mathrm{BSSE}}[\mathrm{HF/pTZ}]-\mathrm{c}2E_{\mathrm{BSSE}}[\mathrm{HF/pDZ}]\\ &\quad +\mathrm{c}3E_{\mathrm{BSSE}}[\mathrm{MP2/pDZ}]-\mathrm{c}3E_{\mathrm{BSSE}}[\mathrm{HF/pDZ}]\\ &\quad +\mathrm{c}4E_{\mathrm{BSSE}}[\mathrm{MP2/pTZ}]-\mathrm{c}4E_{\mathrm{BSSE}}[\mathrm{HF/pTZ}]\\ &\quad -\mathrm{c}4E_{\mathrm{BSSE}}[\mathrm{MP2/pDZ}]+\mathrm{c}4E_{\mathrm{BSSE}}[\mathrm{HF/pDZ}]\\ &\quad +\mathrm{c}5E_{\mathrm{BSSE}}[\mathrm{CCSD/pDZ}]\\ &\quad -\mathrm{c}5E_{\mathrm{BSSE}}[\mathrm{MP2/pDZ}] \qquad (12)\\ &= (\mathrm{c}1-\mathrm{c}2-\mathrm{c}3+\mathrm{c}4)E_{\mathrm{BSSE}}[\mathrm{HF/pDZ}]\\ &\quad +(\mathrm{c}2-\mathrm{c}4)E_{\mathrm{BSSE}}[\mathrm{HF/pTZ}]\\ &\quad +(\mathrm{c}3-\mathrm{c}4-\mathrm{c}5)E_{\mathrm{BSSE}}[\mathrm{MP2/pDZ}]\\ &\quad +\mathrm{c}4E_{\mathrm{BSSE}}[\mathrm{MP2/pTZ}]\\ &\quad +\mathrm{c}5E_{\mathrm{BSSE}}[\mathrm{CCSD/pDZ}], \qquad (13)\end{aligned}$$

where the expressions for the E_{BSSE} at each ab initio level, for example, E_{BSSE}[HF/pDZ] and so forth, are written as in Eq. (8).

The multilevel structure, energy, and Hessian are calculated by using the *Multilevel* program [27]. This program uses the *Gaussian* 98 [28] package to obtain the energy, gradient, and Hessian components and then combines the components to calculate the multilevel energy, gradient, and Hessian. Single-level Hessians were used with the Newton–Raphson step. In most cases, an HF/6-31G(d,p) Hessian was recalculated every three steps, and this matrix was used in the determination of every Newton–Raphson step for all *Multilevel* optimizations. The *Gaussian* 98 [28] package was used separately to obtain the energies of monomers with dimer basis sets.

3 Results and discussion

The structural parameters for H_2O and HF dimer optimized at the multilevel are listed in Tables 1 and 2, which agree quite well with experimental values, although the distances between heavy atoms of H_2O dimer and HF dimer, r_e(OO) and r_e(FF), are slightly shorter and longer than the corresponding experimental values, respectively. However, the structural parameters for the G3 method [optimized at the MP2(full)/6-31G(d) level] show some discrepancy. The β angle of $(H_2O)_2$ is larger than the experimental value. In particular, it was not possible to obtain the correct structure of $(HF)_2$ at the MP2(full)/6-31G(d) level in the standard G3 method, so we have used the MP2(full)/6-31+G(d) level for the geometry optimization and single-point energy calculations were performed based on this structure. We denote it as a G3+ method. The geometrical parameters of $(HF)_2$ at this level are listed in Table 2, which agree quite well with experimental values. The geometrical parameters for $(H_2O)_2$ and $(HF)_2$ optimized at the multilevel depend not only on the computing levels but also the parameter sets [27] used.

The BSSEs and fragment relaxation energies, E_{BSSE} and E_{rel}, for $(H_2O)_2$ and $(HF)_2$ at each ab initio level of the G3 method as shown in Eq. (9), are listed in Table 3. The E_{BSSE}

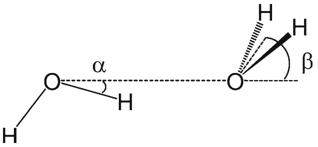

Table 1 The structure of water dimer optimized at various levels of theory (lengths in Å and angles in degree)

Method [a]	r_e(OO)	α	β
MCCM-UT-CCSD(*v2m*)	2.926	3.9	56.9
MCCM-UT-CCSD(*v3s*)	2.927	5.1	55.1
MCCM-UT-CCSD(HCO-*s*)	2.945	5.0	52.6
MCCM-CO-CCSD(T)(*v2m*)	2.900	4.2	56.7
MCCM-CO-CCSD(T)(*v3s*)	2.904	4.9	55.5
MCCM-CO-CCSD(T)(HCO-*s*)	2.943	5.5	54.0
MCG3(*v2m*)	2.945	5.3	54.9
MCG3(*v3s*)	2.933	5.0	55.4
G3	2.913	8.5	77.3
Exp.	2.976[b]	1 ± 10[b]	57 ± 10[b]
	2.946[c]	1 ± 6[c]	58 ± 6[c]

[a] The parameter sets are listed in parentheses
[b] Ref. [33]
[c] Ref. [34]

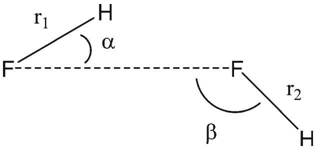

Table 2 The structure of the HF dimer optimized at various levels of theory (lengths in Å and angles in degree)

Method [a]	r_e(FF)	r_1	r_2	α	β
MCCM-UT-CCSD(*v2m*)	2.743	0.924	0.922	7.8	107.7
MCCM-UT-CCSD(*v3s*)	2.756	0.923	0.920	8.1	108.1
MCCM-UT-CCSD(HCO-*s*)	2.785	0.917	0.914	7.3	111.1
MCCM-CO-CCSD(T)(*v2m*)	2.723	0.921	0.919	8.6	105.4
MCCM-CO-CCSD(T)(*v3s*)	2.735	0.921	0.919	8.2	106.7
MCCM-CO-CCSD(T)(HCO-*s*)	2.785	0.917	0.914	7.3	111.1
MCG3(*v2m*)	2.787	0.921	0.920	5.3	115.5
MCG3(*v3s*)	2.781	0.923	0.921	5.1	115.2
G3+ [b]	2.767	0.946	0.944	7.2	114.2
Exp. [c]	2.72			10 ± 6	117 ± 6

[a] The parameter sets are listed in parentheses
[b] MP2(full)/6-31+G(d) level was used for the geometry optimization
[c] Ref. [35]

Table 3 The basis set superposition error (BSSE) and fragment relaxation energies of water and HF dimer at each ab initio level used in the G3 method (energies in kcal/mol. MP2(full)/6-31+G(d) level was used for $(HF)_2$ geometry)

Parameter sets	$(H_2O)_2$		$(HF)_2$	
	E_{BSSE}	E_{rel}	E_{BSSE}	E_{rel}
MP4/6-31+G(d)	2.004	−0.040	1.295	0.013
MP4/6-31G(2df,p)	2.466	0.167	2.991	0.329
MP4/6-31G(d)	2.300	0.015	2.464	0.091
QCISD(T)/6-31G(d)	2.268	0.008	2.398	0.086
MP2(full)/G3large	0.941	0.153	1.056	0.290
MP2/6-31G(2df,p)	2.482	0.174	3.004	0.331
MP2/6-31+G(d)	1.884	−0.025	1.159	0.025
MP2/6-31G(d)	2.215	0.032	2.426	0.103

Table 4 The BSSE and fragment relaxation energies of water dimer at each ab initio level used in the MCG3 method using various parameter sets (energies in kcal/mol)

Parameter sets	*v2m*		*v3s*	
	E_{BSSE}	E_{rel}	E_{BSSE}	E_{rel}
HF/Dd	0.849 (1.128)	0.086 (0.262)	0.861	0.089
HF/MG3(or MG3s)	0.310 (0.400)	0.124 (0.342)	0.427[a]	0.130[a]
MP2/Dd	1.731 (2.215)	−0.031(0.032)	1.758	−0.035
MP2/MG3(or MG3s)	0.871 (0.900)	0.033 (0.143)	0.933[a]	0.034[a]
MP4(SDQ)/Dd	1.685 (2.144)	−0.036(0.026)	1.711	−0.040
MP4(SDQ)/D2dfp	1.914 (2.289)	0.066 (0.181)	1.947	0.069
MP2/D2dfp	2.071 (2.482)	0.066 (0.174)	2.107	0.069
MP4/Dd	1.815 (2.300)	−0.040(0.015)		
QCISD(T)/Dd	1.791 (2.268)	−0.044(0.008)	1.819	−0.049

Numbers in parentheses are from the single point calculations using the MP2(full)/6-31G(d) structures
[a] MG3s basis sets were used instead of the MG3 basis sets

and E_{rel} values depend on the ab initio level used. The BSSE is smallest at the MP2(full)/G3large level and largest at the MP2/6-31G(2df,p) level. In general, the larger the basis sets are, the smaller the BSSE becomes. However, the E_{BSSE} and E_{rel} values in Table 3 are not always the case, for example, the BSSE at MP4/6-31G(2df,p) is larger than that at MP4/6-31G(d,p). This abnormal behavior is not surprising since this BSSE is not computed with the structures optimized at each ab initio level, that is, the structure used is not at its potential energy minimum. Therefore, the BSSE given by Eq. 1 needs not necessarily be smaller when it is computed with larger basis sets. The optimized structure in the G3 method is calculated at the MP2(full)/6-31G(d) level, which is not in the potential energy minimum at other levels, so the fragment relaxation energy using larger basis sets is not necessarily smaller. It is interesting to note that the fragment relaxation energies in some cases have negative values. The BSSE and fragment relaxation energies for $(H_2O)_2$ and $(HF)_2$ at each ab initio level of the MCG3 method are listed in Tables 4 and 5, respectively. The MCG3 method with the *v3s* parameter sets uses the MG3s basis sets instead of the MG3 basis sets and the MP4/Dd level is removed compared with to the MCG3 method with the *v2m* parameter sets [27]. The E_{BSSE} and E_{rel} values at a given ab initio level, e. g. HF/Dd, depend on the parameter sets used. This is not surprising since the optimized structures of monomer and dimer are slightly different depending on the parameter sets, which gives slightly different BSSE and the fragment relaxation energies. Like for the G3 method, the optimized structures at the MCG3 level are not in the potential energy minimum at each ab initio level, therefore the E_{BSSE} and E_{rel} values appear more or less randomly. The fragment relaxation energies are mostly less than 10% of the BSSE except at the MP2(full)/G3large and the HF/MG3 levels in the G3 and the MCG3 methods, respectively. Three parameter sets were used for the MCCM-UT-CCSD and MCCM-CO-CCSD(T) methods. The BSSEs for $(H_2O)_2$ and $(HF)_2$ at each ab initio level of the MCCM-UT-CCSD method, as shown in Eq. (13), are listed in Tables 6 and 7, respectively, and those of the MCCM-CO-CCSD(T) method are listed in Tables 8 and 9, respectively. The equation similar to Eq. (13) for the MCCM-CO-CCSD(T) method is not shown. The fragment relaxation energies are also listed.

Table 5 The BSSE and fragment relaxation energies of HF dimer at each ab initio level used in the MCG3 method using various parameter sets (energies in kcal/mol)

Parameter sets	*v2m*		*v3s*	
	E_{BSSE}	E_{rel}	E_{BSSE}	E_{rel}
HF/Dd	1.404 (1.439)	0.077 (0.903)	1.416	0.094
HF/MG3	0.380 (0.457)	0.218 (1.351)	0.446[a]	0.242[a]
MP2/Dd	2.345 (2.426)	−0.143(0.166)	2.369	−0.137
MP2/MG3	0.959 (1.000)	0.006 (0.635)	0.962[a]	0.019[a]
MP4(SDQ)/Dd	2.274 (2.349)	−0.143(0.164)	2.298	−0.137
MP4(SDQ)/D2dfp	2.717 (2.834)	0.057 (0.804)	2.748	0.073
MP2/D2dfp	2.876 (3.004)	0.044 (0.762)	2.909	0.059
MP4/Dd	2.383 (2.464)	−0.151(0.135)		
QCISD(T)/Dd	2.321 (2.398)	−0.154(0.123)	2.345	−0.149

Numbers in parentheses are from the single point calculations using the MP2(full)/6-31+G(d) structures
[a] MG3s basis sets were used

Not only the optimized structures but also E_{BSSE} and E_{rel} values at a given ab initio level depend on the parameter sets used. The fragment relaxation energies are quite small, and have negative values in some cases.

The dimerization energies of the water dimer with and without the BSSE correction at various multilevels are listed in Table 10. The dimerization energies without the BSSE, E_{D}, agree almost perfectly with the experimental value at the MCCM-UT-CCSD and MCCM-CO-CCSD(T) levels using the *v2m* parameter sets. The E_{D} values using the *v3s* parameter sets are slightly smaller. The E_{BSSE} values for the G3 method are obtained by Eq. (9), and those at the multilevel are obtained by expressions like Eq. (13) of the MCCM-UT-CCSD, that is, these E_{BSSE} values are the result of linear combination of the E_{BSSE} at each ab initio level multiplied by empirical parameters. The smallest and the largest E_{BSSE} values are 0.046 kcal/mol at the MCCM-UT-CCSD(HCO-*s*) level and 0.976 kcal/mol at MCCM-UT-CCSD(*v2m*), respectively. The BSSE at the G3 level is 0.929 kcal/mol. The fragment relaxation energies are quite small in most cases (smaller than 0.04 kcal/mol) except for the G3 method. The largest error in the dimerization energy of $(H_2O)_2$ due to the BSSE is about 22% for the multilevel studied in this paper [MCCM-UT-CCSD(*v2m*)]. It is 22% in the case of the G3 too. This is

Table 6 The BSSE and fragment relaxation energies of water dimer at each ab initio level used in the MCCM-UT-CCSD method using various parameter sets (energies in kcal/mol)

Parameter sets	*v2m*		*v3s*		HCO-*s*	
	E_{BSSE}	E_{rel}	E_{BSSE}	E_{rel}	E_{BSSE}	E_{rel}
HF/pDZ	2.046	0.132	2.003 (2.312)	0.127 (0.301)	1.934	0.096
HF/pTZ	0.827	0.143	0.811 (0.921)	0.129 (0.348)	0.789	0.107
MP2/pDZ	3.349	0.036	3.264 (3.850)	0.044 (0.123)	3.127	−0.001
MP2/pTZ	1.636	0.040	1.598 (1.834)	0.039 (0.157)	1.540	0.003
CCSD/pDZ	3.139	0.029	3.061 (3.592)	0.036 (0.117)	2.936	−0.008

Numbers in parentheses are from the single point calculations using the MP2(full)/6-31G(d) structures

Table 7 The BSSE and fragment relaxation energies of HF dimer at each ab initio level used in the MCCM-UT-CCSD method using various parameter sets (energies in kcal/mol)

Parameter sets	*v2m*		*v3s*		HCO-*s*	
	E_{BSSE}	E_{rel}	E_{BSSE}	E_{rel}	E_{BSSE}	E_{rel}
HF/pDZ	1.900	0.252	1.864 (1.821)	0.231 (1.202)	1.900	0.550
HF/pTZ	0.654	0.300	0.645 (0.628)	0.278 (1.324)	0.654	0.678
MP2/pDZ	3.033	0.016	2.965 (2.894)	−0.003(0.592)	3.033	−0.078
MP2/pTZ	1.358	0.036	1.331 (1.294)	0.017 (0.641)	1.358	−0.024
CCSD/pDZ	2.888	0.024	2.823 (2.756)	0.005 (0.610)	2.888	−0.055

Numbers in parentheses are from the single point calculations using the MP2(full)/6-31+G(d) structures

Table 8 The BSSE and fragment relaxation energies of water dimer at each *ab initio* level used in the MCCM-CO-CCSD(T) method using various parameter sets (energies in kcal/mol)

Parameter sets	*v2m*		*v3s*		HCO-*s*	
	E_{BSSE}	E_{rel}	E_{BSSE}	E_{rel}	E_{BSSE}	E_{rel}
HF/pDZ	2.085	0.127	2.052	0.132	1.947	0.100
HF/pTZ	0.836	0.140	0.825	0.140	0.793	0.112
MP2/pDZ	3.418	0.018	3.355	0.034	3.152	−0.006
MP2/pTZ	1.662	0.024	1.635	0.034	1.549	−0.000
CCSD/pDZ	3.206	0.011	3.147	0.026	2.958	−0.013
CCSD/pTZ	1.450	0.033	1.428	0.041	1.354	0.009
CCSD(T)/pDZ	3.349	0.006	3.287	0.022	3.087	−0.018
CCSD(T)/pTZ	1.572	0.019	1.547	0.029	1.465	−0.004

Table 9 The BSSE and fragment relaxation energies of HF dimer at each ab initio level used in the MCCM-CO-CCSD(T) method using various parameter sets (energies in kcal/mol)

Parameter sets	*v2m*		*v3s*		HCO-*s*	
	E_{BSSE}	E_{rel}	E_{BSSE}	E_{rel}	E_{BSSE}	E_{rel}
HF/pDZ	1.958	0.234	1.920	0.236	1.768	0.150
HF/pTZ	0.700	0.287	0.659	0.288	0.618	0.195
MP2/pDZ	3.140	−0.026	3.068	−0.019	2.789	−0.069
MP2/pTZ	1.402	−0.003	1.373	0.002	1.255	−0.050
CCSD/pDZ	2.986	−0.017	2.922	−0.010	2.657	−0.061
CCSD/pTZ	1.269	0.035	1.244	0.040	1.139	−0.018
CCSD(T)/pDZ	3.094	−0.029	3.028	−0.022	2.751	−0.071
CCSD(T)/pTZ	1.379	0.007	1.351	0.013	1.232	−0.041

not a trivial error, so one should consider the BSSE carefully in order to predict the dimerization energy accurately.

It is also interesting to note that the E_{BSSE} values depend on the parameter sets. When the HCO-*s* parameter sets are used, the MCCM-UT-CCSD level gives the smallest E_{BSSE} value, which is 0.046 kcal/mol. The E_{rel} value is 0.032 kcal/mol, so the pure basis set effect without the geometry relaxation term is only 0.014 kcal/mol at this level. However, at the MCCM-CO-CCSD(T) level, the E_{BSSE} value becomes quite larger, which is quite unusual. The MCCM-UT-CCSD method is a subset of the MCCM-CO-CCSD(T), that is, the latter has more terms and coefficients for the higher level of ab initio theory than the former [27]. So the latter gives better results than the former in general. Using the *v2m* and *v3s* parameter sets, the higher level [MCCM-CO-CCSD(T)] gives smaller E_{BSSE} value than the lower level (MCCM-UT-CCSD). The *v3s* parameter sets give smaller E_{BSSE} value than the *v2m* in the same level except for the MCG3. Table 11 lists the coefficients of Eq. (13) for the parameter sets used in the MCCM-UT-CCSD method. The coefficients from the HCO-*s* parameter sets seem somewhat different from others. The coefficients of the first- and second terms have opposite sign and the c5 value is quite small. The BSSE depending on the parameter sets suggests that it may be reduced further by adjusting the parameters.

After the BSSE correction, the dimerization energy, E_{corr}, at the MCCM-CO-CCSD(T)(*v3s*) level agrees best with the experimental value, followed by that at the MCCM-CO-CCSD (T)(*v2m*) level. Three E_{corr} values are within the experimental error limit. The dimerization energies of the HF dimer with and without the BSSE correction at various multilevels are listed in Table 12. The E_{BSSE} value is largest at the G3+ level and smallest at the MCCM-CO-CCSD(T)(*v3s*) level. The E_{corr} value at the MCCM-CO-CCSD(T)(*v3s*) level agrees best with the experimental value. Note that MCG3 values agree slightly better with the experimental value than the G3+ value before the BSSE correction, however, after the correction the G3+ value agrees slightly better, although it contains larger BSSE. For both $(H_2O)_2$ and $(HF)_2$ the MCCM-CO-CCSD(T)(*v3s*) level predicts the best E_{corr} value. Tables 10

Table 10 Dimerization energies of the water dimer with and without the BSSE correction at various levels of theory (energies in kcal/mol)

Method[a]	E_D	E_{BSSE}	E_{rel}	E_{corr}
MCCM-UT-CCSD(*v2m*)	−5.42	0.976 (1.426)	0.028 (0.032)	−4.47
MCCM-UT-CCSD(*v3s*)	−5.18	0.431 (1.396)	0.032 (0.031)	−4.75
MCCM-UT-CCSD(*v3s*)-SP[b]	−4.99	0.381 (1.577)	0.167 (0.151)	−4.61
MCCM-UT-CCSD(HCO-*s*)	−4.72	0.046 (1.348)	0.032(−0.003)	−4.67
MCCM-CO-CCSD(T)(*v2m*)	−5.40	0.604 (1.572)	0.034 (0.019)	−4.80
MCCM-CO-CCSD(T)(*v3s*)	−5.30	0.245 (1.547)	0.035 (0.029)	−5.05
MCCM-CO-CCSD(T)(HCO-*s*)	−4.72	0.714 (1.465)	0.007(−0.004)	−4.00
MCG3(*v2m*)	−4.92	0.806 (0.820)	0.023 (0.025)	−4.11
MCG3(*v2m*)-SP[b]	−4.62	0.744 (0.831)	0.127 (0.131)	−3.85
MCG3(*v3s*)	−5.06	0.885 (0.882)	0.024 (0.025)	−4.18
G3	−5.14	0.929	0.141	−4.22
Exp.[c]				−5.44 ± 0.7

Numbers in brackets are calculated with 1 for all parameters of the multilevel

[a] The parameter sets are listed in parentheses

[b] Single point calculations using the MP2(full)/6-31G(d) structures

[c] Ref. [33]

Table 11 Coefficients of Eq. (13) for the parameter sets used in the MCCM-UT-CCSD method

	v2m	*v3s*	HCO-*s*
c1 − c2 − c3 + c4	0.1547	0.6562	−0.0294
c2 − c4	−0.2188	−0.5987	0.2752
c3 − c4 − c5	−1.2515	−1.7643	−0.8953
c4	1.4813	1.9995	1.6133
c5	0.8312	0.7073	0.0687

and 12 have shown that the multilevel method with smaller BSSE does not automatically give the better dimerization energies.

The G3 calculations use MP2(full)/6-31G(d) and MP2 (full)/6-31+G(d) structures for $(H_2O)_2$ and $(HF)_2$, respectively, while the MCCM uses the structures optimized at its own level. The MCCM parameters were adjusted to reproduce atomization energies using MP2/6-31G(d) structures. So, it would be interesting to compare the BSSEs of the G3 with those of the MCCM using the same structure. We took the structures used for the G3 calculations, and performed the MCG3(*v2m*) and MCCM-UT-CCSD(*v3s*) level calculations. The BSSEs at each ab initio level used in the MCG3(*v2m*) are listed in Tables 4 and 5 (numbers in parentheses) for $(H_2O)_2$ and $(HF)_2$, respectively, and those for the MCCM-UT-CCSD are listed in Tables 6 and 7 (numbers in parentheses) for $(H_2O)_2$ and $(HF)_2$, respectively. The E_{BSSE} values become slightly larger in all cases. Interestingly, all E_{rel} values become positive. The dimerization energies and the BSSE correction are listed in Tables 10 and 12 for $(H_2O)_2$ and $(HF)_2$, respectively. The difference in the dimerization energy for $(H_2O)_2$ with and without geometry optimization is quite small (6% for MCG3 and 4% for MCCM-UT-CCSD). Note that the E_{BSSE} values become smaller (4% for MCG3 and 12% for MCCM-UT-CCSD) without optimization, although these values at each ab initio level of the MCCM-UT-CCSD are all larger as shown in Tables 4, 5, 6, and 7. These values need not be necessarily larger since the final E_{BSSE} values in the dimerization energy are obtained from each ab initio E_{BSSE} values by the multiplying parameters. The MCCM parameters were adjusted to reproduce the atomization energies using the MP2/6-31G(d) structures, so they might be concurrently optimized to give small BSSEs as well. The difference in the dimerization energy for $(HF)_2$ with and without geometry optimization is also quite small (10% for MCG3 and 8% for MCCM-UT-CCSD). In this case, the E_{BSSE} value without optimization is slightly larger (∼5%) for the MCG3, but smaller (∼5%) for the MCCM-UT-CCSD. These results imply that single-point MCCM predicts slightly smaller dimerization energies in general with reasonably small BSSEs.

In order to understand the role of the empirical parameters for the MCCM, we have calculated the BSSE without scaling (set all coefficients to 1), and the results are listed in Tables 10 and 12 (numbers in brackets). Since the optimized structures depend on the parameter sets, the BSSEs without scaling are slightly different depending on the parameter sets. The BSSEs for all MCCMs except MCG3 are greatly increased by setting all coefficients to 1, which means that the empirical parameters do reduce the BSSE significantly. However, the BSSE of the MCG3 is reduced only slightly, which means that, for this method, most of it remains. It is also interesting to note that the BSSE of G3 is slightly larger than that of MCG3 without scaling.

The dimerization energies with CP correction in Table 10 and 12 are all larger (weaker interaction) than those without, which are therefore further off from the experimental values. In some cases where the BSSE is really small (smaller than experimental error), in which most part of the BSSE seems to be absorbed into the empirical parameter, one may be able to calculate dimerization energy without the CP correction. It has been pointed out that the CP correction overestimates the BSSE [29–31], and the better way might be to use the largest basis sets affordable without the CP-correction [32]. Therefore, it might be possible to reproduce dimerization energies within chemical accuracy using an MCCM with good empirical parameters without the CP correction.

Table 12 Dimerization energies of HF dimer with and without the BSSE correction at various levels of theory (energies in kcal/mol)

Method [a]	E_D	E_{BSSE}	E_{rel}	E_{corr}
MCCM-UT-CCSD(*v2m*)	−4.85	0.763 (1.214)	0.027 (0.044)	−4.08
MCCM-UT-CCSD(*v3s*)	−4.55	0.264 (1.189)	0.028 (0.025)	−4.29
MCCM-UT-CCSD(*v3s*)-SP[b]	−4.17	0.250 (1.156)	0.665 (0.660)	−3.92
MCCM-UT-CCSD(HCO-*s*)	−4.03	0.201 (1.214)	0.198(−0.001)	−4.22
MCCM-CO-CCSD(T)(*v2m*)	−4.73	0.420 (1.379)	0.034 (0.007)	−4.31
MCCM-CO-CCSD(T)(*v3s*)	−4.58	0.087 (1.351)	0.033 (0.013)	−4.49
MCCM-CO-CCSD(T)(HCO-*s*)	−4.03	0.487 (1.232)	−0.017(−0.041)	−3.54
MCG3(*v2m*)	−4.36	0.706 (0.846)	0.017 (0.008)	−3.65
MCG3(*v2m*)-SP[b]	−3.93	0.743 (0.880)	0.667 (0.636)	−3.19
MCG3(*v3s*)	−4.41	0.752 (0.848)	0.018 (0.021)	−3.66
G3+	−4.93	1.075	0.284	−3.85
Exp. [c]				−4.63 ± 0.17

Numbers in brackets are calculated with 1 for all parameters of the multilevel

[a] The parameter sets are listed in parentheses

[b] Single point calculations using the MP2(full)/6-31+G(d) structures

[c] Ref. [36]

4 Conclusions

The E_{BSSE} values for $(H_2O)_2$ and $(HF)_2$ are 0.05–0.98 and 0.20–1.10 kcal/mol, respectively, depending on the level of theory and the parameter sets used. This is not a trivial error, so one might need to consider the BSSE carefully in order to predict the dimerization energy accurately. In some cases, the empirical parameters for MCCMs do reduce the BSSE a lot, although one cannot ignore the BSSE completely. The MCCMs with the *v3s* parameter sets have better agreement with experiments and give smaller BSSEs than those with the *v2m* parameter sets. The best BSSE-corrected dimerization energies are obtained at the MCCM-CO-CCSD(T)(*v3s*) level for both $(H_2O)_2$ and $(HF)_2$, and the E_{BSSE} values are 0.25 and 0.09 kcal/mol, respectively. These BSSEs introduce 5 and 2% errors, respectively. However, the MCCM-CO-CCSD(T) level is quite expensive, so only small molecular system would be affordable to do. The MCCM-UT-CCSD(*v3s*) level also gives quite good results in the dimerization energies, and the BSSEs generate 8 and 6% errors for $(H_2O)_2$ and $(HF)_2$, respectively. The G3 method produces about 1 kcal/mol of BSSE. The multilevel methods giving the smaller BSSE do not automatically give the better dimerization energies. Further optimization for the parameter sets would be necessary to obtain the best E_{corr} value with the minimal BSSE. It might be possible to reproduce dimerization energies within chemical accuracy using an MCCM with good empirical parameters without the CP correction.

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