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# On the origin of spurious errors in many-body expansion for water cluster[†]

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**Abstract.**   Many-body expansion (MBE) has been carried out to investigate two- to five-body energy terms and their contributions to the interaction energy (IE) of $(H_2O)_{15}$ cluster. We have observed that the erroneous contribution of many-body terms on IE originated from cheaper convergence thresholds set as default in popular quantum mechanics packages. The propagation of errors from smaller to higher-body terms, due to the combinatorial nature of MBE, is also observed.

**Keywords.**   Interaction energy; many-body expansion; $(H_2O)_{15}$; SCF convergence criteria; integration grid.

## 1. Introduction

Formation of clusters of varying size is a topic of outstanding contemporary interest. Non-covalent interactions, which determine the structure, function and properties of supramolecular assemblies, mutually influence each other in a cooperative or anti-cooperative fashion.[1–9] The idea of cooperativity in non-covalent interactions may be traced from the 'non-additive' terms (i.e., three-, four- and higher-body terms) of many-body expansion (MBE).[10,11] MBE is a unique canonical supermolecular approach, where the total energy or interaction energy (IE) of a large system—is often calculated as the sum of one-body, two-body up to $x$-body energy contributions. In order to model large systems, a variety of fragmentation methods[12–14] have been introduced based by truncating MBE appropriately. Water is one of the most extensively studied systems, for the last 60 years starting from the novel observation on cooperative nature of water cluster by Frank and Wen in 1957.[15] The applicability of MBE for the molecular clusters was first reported by Hankins and Moskowitz in order to explain the cooperativity of $(H_2O)_{2-3}$.[16,17] Earlier studies have shown that the three-body term contributes significantly to the IE for water clusters, while the contribution of four-body effect is found to be small.[10,18–20] In order to address the effect of many-body terms for

$(H_2O)_{2-6}$ water clusters, it has been found that three-body term is essential to describe the IE.[21,22] It has been shown that the magnitude of contribution for $x$-body terms decreases as $x$ increases and therefore the contribution of four- and higher order terms becomes smaller and smaller.[18,21–23] The truncation of MBE is now well acceptable in simulation studies, as these studies often truncate MBE into three-body term.[24] The urge for inclusion of long-range four- and higher-body interactions in simulation studies are also being suggested.[25,26] It was also proposed that there is a need to explore the role of higher-order terms in order to parameterize the potential for water.[27,28] The knowledge of these *ab-initio* calculations on the MBE is helpful for evaluating the existing and developing new interaction potential for water.[29] However, studies beyond four-body term on large water clusters[30–36] are scarce, despite enormous studies on this topic.[10,11,16–18] Non-additivity of interaction energy in a supramolecular assembly,[37–49] comprising non-covalent interactions, has become a topic of fundamental interest. This anomalous property of non-additivity can potentially be a causative factor for erroneous propagation of $x$-body terms in MBE. The influence of non-additivity on molecular hyperpolarizability is also being explored.[50,51] Therefore, it is important to note that the MBE analysis is utilized in various significant methodological approaches. However, since MBE is of combinatorial nature (i.e., higher order terms require the information of lower order terms), a small error might bring in spurious error in higher order terms. Herein, we have undertaken an

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[†]Dedicated to the memory of the late Professor Charusita Chakravarty.

exhaustive and systematic study to test the influence of self-consistent field (SCF) convergence criteria on MP2, HF and B3LYP methods for MBE, taking $(H_2O)_{15}$ as a test case.[52]

## 2. Computational methods

According to Kaplan and co-workers,[53,54] the $x$-body energy terms of $n$-mer system can be obtained as,

$$\Delta E^{IE}(1, 2, \ldots n) = \sum_{i<j<k<l<m\ldots<x} \Delta^x E(i, j, k, l, m \ldots x)$$
$$- \sum_c^{x-1} a_{x(n)}^c \Delta^c E(n) \quad (1)$$

where,

$$a_{x(n)}^c = \frac{(n-c)!}{(n-x)!(x-c)!} \quad (2)$$

The two-body ($\Delta^2 E(1, 2, \ldots 15)$) contributions to the interaction energy for 15-mer system (i.e., $(H_2O)_{15}$) can be derived from equation (1):

$$\Delta^2 E(1, 2, \ldots 15) = \sum_{i<j} E(i, j) - a_{2(15)}^1 \sum_i E(i)$$
$$= \sum_{i<j} E(i, j) - 14 \sum_i E(i) \quad (3)$$

Similarly, three- to five-body (i.e., $\Delta^3 E(1, 2, \ldots 15), \Delta^4 E(1, 2, \ldots 15)$ and $\Delta^5 E(1, 2, \ldots 15)$) terms for 15-mer system can be written as follows:

$$\Delta^3 E(1, 2, \ldots 15) = \sum_{i<j<k} E(i, j, k) - a_{3(15)}^1 \sum_i E(i)$$
$$- a_{3(15)}^2 \sum_{i<j} \Delta^2 E(i, j)$$
$$= \sum_{i<j<k} E(i, j, k) - 91 \sum_i E(i) - 13 \sum_{i<j} \Delta^2 E(i, j)$$
$$\quad (4)$$

$$\Delta^4 E(1, 2, \ldots 15)$$
$$= \sum_{i<j<k<l} E(i, j, k, l) - a_{4(15)}^1 \sum_i E(i)$$
$$- a_{4(15)}^2 \sum_{i<j} \Delta^2 E(i, j) - a_{4(15)}^3 \sum_{i<j<k} \Delta^3 E(i, j, k)$$
$$= \sum_{i<j<k<l} E(i, j, k, l) - 364 \sum_i E(i) - 78 \sum_{i<j} \Delta^2 E(i, j)$$
$$- 12 \sum_{i<j<k} \Delta^3 E(i, j, k) \quad (5)$$

and

$$\Delta^5 E(1, 2, \ldots 15)$$
$$= \sum_{i<j<k<l<m} E(i, j, k, l, m) - a_{5(15)}^1 \sum_i E(i)$$

$$- a_{5(15)}^2 \sum_{i<j} \Delta^2 E(i, j) - a_{5(15)}^3 \sum_{i<j<k} \Delta^3 E(i, j, k)$$
$$- a_{5(15)}^4 \sum_{i<j<k<l} \Delta^4 E(i, j, k, l)$$
$$= \sum_{i<j<k<l<m} E(i, j, k, l, m) - 1001 \sum_i E(i)$$
$$- 286 \sum_{i<j} \Delta^2 E(i, j) - 66 \sum_{i<j<k} \Delta^3 E(i, j, k)$$
$$- 11 \sum_{i<j<k<l} \Delta^4 E(i, j, k, l) \quad (6)$$

To understand the effect of many-body in $(H_2O)_{15}$ (Figure S1, in Supplementary Information), the optimization of the cluster has been done at MP2, HF and B3LYP levels of theory augmented with 6-311+G* basis set, followed by frequency calculation. The choice of the basis set for the current study has been done based on our laboratory's previous work.[30] Neela *et al.*,[30] have extensively studied the basis set dependence on IE for different arrangements of water cluster with varying size (i.e., $n = 2$–20). Using various basis sets, *viz*, 6-31G*, 6-31G**, 6-311+G*, 6-311++G**,cc-pVDZ, aug-cc-pVDZ, cc-pVTZ, and aug-cc-pVTZ, they have observed that variation in IE is very minor in the case of 6-311+G*.[30] The widely used B3LYP method was chosen for the current study as B3LYP can provide reasonable optimize geometry for non-covalent systems than other functional, *viz.*, B97-D, $\omega$B97X-D, and M06-2X.[55]

Throughout this study, the geometry of the various subsystems has been taken from the respective optimized system, followed by single point calculations at the aforementioned levels of theory to compute extensively all the energy values for subsystems. All the geometry optimizations were systematically carried out using the default criteria, i.e., for HF, MP2 calculations 'tight' SCF ('SCF = tight', which is synonymous with 'convergence = N'; N being 8 for geometry optimization and frequency calculations and N = 4 for single point calculations) and for B3LYP level 'fine' grid (i.e., 75 radial shells and 302 angular points per shell) were used. Initially, in the case of single point calculations for all the methods (i.e., MP2, HF and B3LYP), we have followed the default criteria.

In order to investigate whether SCF convergence criteria has any impact on $x$-body ($x = 2$ to 5) calculations at MP2 and HF levels or not, we have computed all the energy values for subsystems present in $(H_2O)_{15}$ by using the tighter SCF convergence criteria. The tighter SCF convergence criteria at MP2/6-311+G* and HF/6-311+G* levels of theory have been achieved by performing 'convergence = 10' for the single point calculations. The tighter quality criteria at B3LYP/6-311+G* level of theory has been achieved by performing two different higher-order integration grid calculations, i.e., 'UltraFine' (UF) and 'SuperFineGrid' (SF). The UF grid is a pruned grid which consists 99 radial shells and 590 angular points per shell, whereas, SF grid is almost three times larger than UF by defining 150 radial shells and 974 angular points per shell. The use of such high criteria (i.e., using 'convergence = 10' for HF and MP2 and UF and SF for

B3LYP) has added significant cost for computing the individual subsystem calculations. Moreover, to obtain the $x$-body energy of $(H_2O)_{15}$ one needs to compute $15!/(x!(15-x)!)$ calculations.[52–54] It is worthwhile to mention here that MBE calculations depend on '$x$'-body energy terms as well as the cluster size ($n$). Therefore, in view of the steep increase in computational cost, we restricted our calculations up to five-body (i.e., $x = 5$) energy terms for $(H_2O)_{15}$ (i.e., $n = 15$) water cluster.[52] The basis set superposition error (BSSE) was estimated using counter poise technique.[56] Indeed, the usefulness of BSSE correction is a controversial topic, which is described elsewhere.[57–59] All the calculations were performed using Gaussian 09 program.[60]

## 3. Results and Discussion

The IE and $x$-body ($x = 2$–5) energy terms (with and without BSSE correction) for $(H_2O)_{15}$ as obtained at MP2/6-311+G* level of theory with above mentioned different SCF convergence criteria, are presented in Table 1. Comparing the results of default and 'convergence = 10' calculations (derived from without BSSE correction results), we have observed that the influence of SCF convergence criteria on IE and two-body energy term at MP2 level seems to be negligible (Table S1 in SI, also). For two-body term, up to seven decimal points in hartree, there are no changes observed between default and 'convergence = 10' values. In the cases of three- to four- to five-body terms, the change between default and 'convergence = 10' values occurred at six, five and four decimal points in hartree, respectively. The BSSE-corrected $x$-body values also show small change in the values between default and 'convergence = 10' criteria. Although, these small variations of IE and $x$-body energy values with convergence criteria have almost no effect on the percentage contribution of $x$-body terms (Table S2 in SI), it is informing us that because of the combinatorial nature of MBE, the error is propagating from two- to five-body terms. These accumulated errors may eventuate in an erroneous result for higher body terms or may even become problematic to calculate for large systems, as MBE is a combinatorial function of both truncation order ($x$) as well as system size.

Table 1 shows that HF method is less vulnerable with the convergence criteria than MP2 method. Almost up to eight decimal points of the energy in hartrees there are no changes in the values of $x$-body ($x = 2$–5) terms by applying higher SCF convergence criteria for HF method in both the cases (with and without BSSE corrected energy terms). As a result, there are no variations in the percentage contributions of $x$-body terms to IE (Table S2 in SI). However, it has been shown earlier that

HF method can qualitatively describe the variation of $x$-body terms, but it produces quantitatively large errors in two-body level.[21] As a result, it is not adequate in the canonical supermolecular approach, like MBE.[61]

Table 1 also represents default, UF and SF results as obtained at B3LYP/6-311+G* level of theory for the interaction energy and $x$-body ($x = 2$–5) energy terms, with and without BSSE correction, of $(H_2O)_{15}$ (see Table S1 in SI, also). We have observed that B3LYP/6-311+G* results with default criteria are erroneous, particularly for higher-order terms. For instance, the percentage contribution of five-body term ($-13.2\%$) to IE for $(H_2O)_{15}$ is questionable, whereas, the percentage contributions of two-, three- and four-body terms are 86.1%, 10.9% and 7.5% (Table S2 in SI). The signs of percentage contribution can either be positive corresponding to attractive contribution or negative indicating repulsive contribution as observed earlier.[21–23] Generally, for water clusters the contribution for higher order terms decreases with increasing $x$.[18,21–23] But the observed percentage contribution of five-body effect to IE is higher than four- and even three-body terms. When attempting to compute counter poise-corrected IE and $x$-body terms for $(H_2O)_{15}$, the magnitude of five-body contribution decreased to 9.4%, which however, is also a counterfactual result as this is higher than the four-body contribution (4.6%). Although earlier studies have shown that as the contribution of higher-body term decreases with increasing the randomness in long-range molecular orientations.[23] Recently, it has been shown that by tightening the integration grid size one can improve four- and five-body terms.[62,63] In our study, we have also observed that IE values as obtained from default, UF and SF calculations are virtually identical. Similar observation has also been made for BSSE-corrected IE values. For two-body energy term (for both the cases, i.e., with and without BSSE correction), the difference between default and UF (and/or SF) value remains <1 kcal/mol (0.0003 hartree, which is almost equivalent to 0.2 kcal/mol). However, the differences between default and UF (and/or SF) values are increasing (for both the cases, i.e., with and without BSSE correction) with increasing from three- to four-body energy terms. Finally, for five-body term, it reaches to 0.03 hartree (i.e., about 19.0 kcal/mol) in the case of without BSSE correction, while, with BSSE correction, these differences are 0.02 hartree (i.e., approximately 15.6 kcal/mol) (Table S1 in SI). The improvements are also noticed while using the SF approach in $(H_2O)_{15}$ cluster calculation. Although, the $x$-body energy differences in $(H_2O)_{15}$ between UF and SF do not manifest any significant values (maximum difference as observed

**Table 1.** The interaction energy and $x$-body ($x = 2$–5) energy terms (with and without BSSE correction) for $(H_2O)_{15}$ as obtained at different levels of theory[a] with different convergence criteria (for details, see the text). The energy values are in hartree. Subscripted values are $10^{-5}$ hartree.

| Method | | IE | 2-body | 3-body | 4-body | 5-body |
|---|---|---|---|---|---|---|
| MP2 | Energy (default) | $-0.339645_{2878}$ | $-0.297321_{4741}$ | $-0.037547_{5466}$ | $-0.011307_{8958}$ | $0.012073_{7068}$ |
| | Energy (convergence = 10) | $-0.339645_{2726}$ | $-0.297321_{4843}$ | $-0.037547_{9355}$ | $-0.011305_{3959}$ | $0.012057_{5915}$ |
| | Energy (BSSE) (default) | $-0.227662_{9951}$ | $-0.176160_{4287}$ | $-0.049303_{7579}$ | $-0.002233_{1537}$ | $-0.000051_{16244}$ |
| | Energy (BSSE) (convergence =10) | $-0.227662_{9312}$ | $-0.176160_{3866}$ | $-0.049304_{3965}$ | $-0.002329_{9686}$ | $-0.000047_{36071}$ |
| HF | Energy (default) | $-0.247686_{7528}$ | $-0.228831_{0529}$ | $-0.014636_{8789}$ | $-0.007911_{7585}$ | $0.006987_{9470}$ |
| | Energy (convergence=10) | $-0.247686_{7561}$ | $-0.228831_{0557}$ | $-0.014636_{8763}$ | $-0.007911_{7697}$ | $0.006987_{9806}$ |
| | Energy (BSSE) (default) | $-0.203688_{5528}$ | $-0.178185_{7808}$ | $-0.023878_{1956}$ | $-0.001669_{0934}$ | $-0.000217_{17446}$ |
| | Energy (BSSE) (convergence =10) | $-0.203688_{5561}$ | $-0.178185_{7835}$ | $-0.023878_{1930}$ | $-0.001669_{1007}$ | $-0.000217_{17464}$ |
| B3LYP | Energy (default) | $-0.319428_{6812}$ | $-0.275133_{7903}$ | $-0.034877_{2568}$ | $-0.024009_{9051}$ | $0.042173_{1074}$ |
| | Energy (UF[b]) | $-0.319396_{6955}$ | $-0.274812_{1781}$ | $-0.037234_{4811}$ | $-0.013493_{4998}$ | $0.011398_{5739}$ |
| | Energy (SF[c]) | $-0.319402_{5973}$ | $-0.274814_{9476}$ | $-0.037216_{6975}$ | $-0.013559_{4843}$ | $0.011505_{76301}$ |
| | Energy (BSSE) (default) | $-0.262883_{0588}$ | $-0.207227_{5983}$ | $-0.050706_{84364}$ | $-0.012114_{09644}$ | $0.024717_{99361}$ |
| | Energy (BSSE) (UF[b]) | $-0.262873_{6702}$ | $-0.206915_{8637}$ | $-0.052885_{1866}$ | $-0.003396_{5078}$ | $-0.000087_{9006}$ |
| | Energy (BSSE) (SF[c]) | $-0.262873_{5878}$ | $-0.206918_{5072}$ | $-0.052886_{7688}$ | $-0.003473_{7419}$ | $0.000178_{5161}$ |

[a]All values are computed using 6-311+G* basis set. [b]UF corresponds to 'UltraFine' grid; i.e., 99 radial shells x 590 angular points.
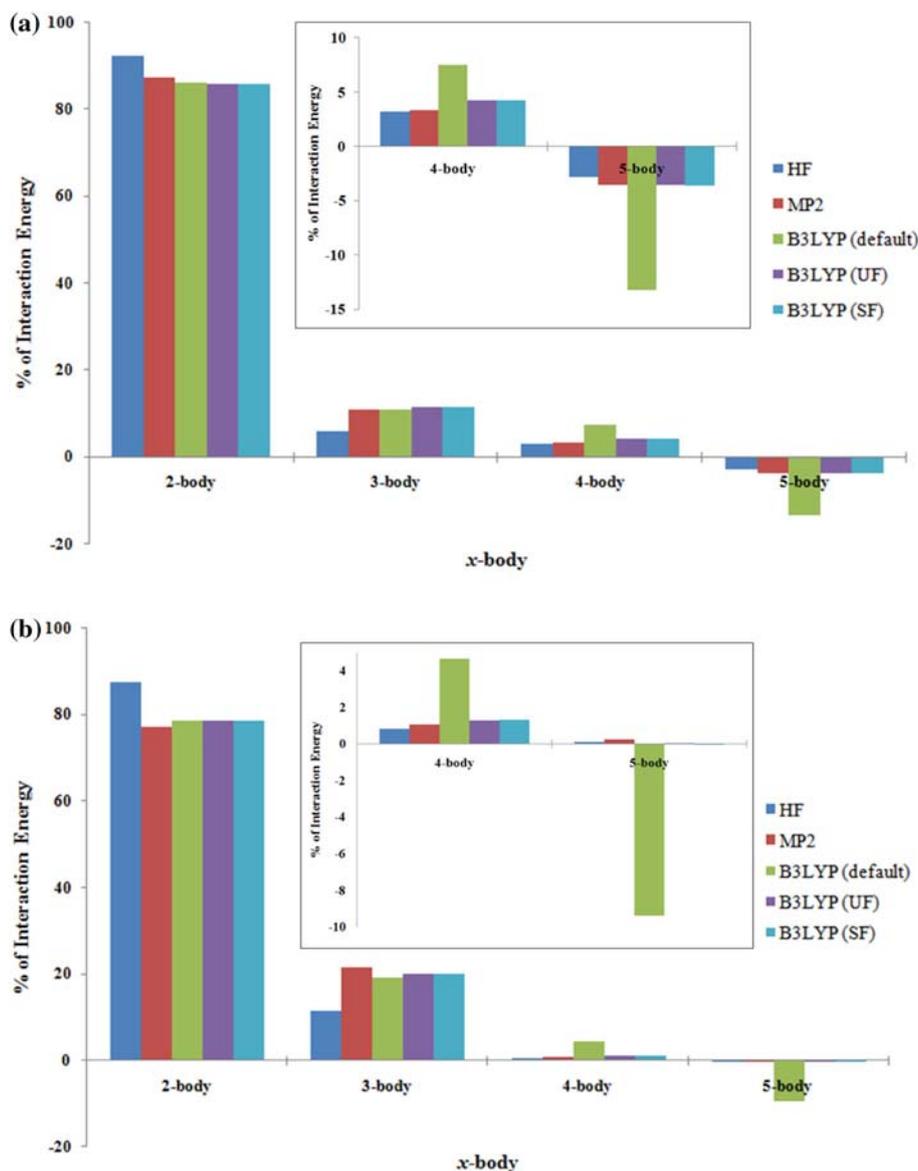[c]SF corresponds to 'SuperFineGrid'; i.e., 150 radial shells x 974 angular points.

**Figure 1.** Variation of percentage contribution: (a) without BSSE correction, and (b) with BSSE correction for $x$-body ($x = 2$–5) energy terms to the interaction energy as obtained at different methods of theory with 6-311+G* basis set in the case of $(H_2O)_{15}$. UF corresponds to 'UltraFine' grid; i.e., 99 radial shells x 590 angular points while SF corresponds to 'SuperFineGrid'; i.e., 150 radial shells x 974 angular points.

in the case of five-body term is 0.0001 hartree for without BSSE corrected results), but a precision better than $10^{-6}$ hartree is required for higher-body terms, as shown earlier.[62,63]

Our observed circumstances are represented in Figure 1, which shows the percentage contribution of $x$-body terms to IE plot, where MP2 and HF default results are compared with B3LYP-default, B3LYP-UF and B3LYP-SF. The default $x$-body values of HF and MP2 results are considered, since we have found that the percentage contribution of $x$-body energy terms

are same while changing the SCF convergence criteria from default to 'convergence = 10'. The observed two-body contributions, without BSSE corrections (Figure 1(a)), are 92.4%, 87.5%, 86.1%, 86.0% and 86.0% for HF, MP2, B3LYP-default, B3LYP-UF and B3LYP-SF calculations, respectively, whereas, for three-body case, the percentage contributions are 5.9%, 11.1%, 10.9%, 11.7% and 11.7%, respectively (Table S2 in SI). However, the higher precisions for two- and three-body terms obtained by using higher order grids for B3LYP method are insignificant in the case of $(H_2O)_{15}$.

Figure 1(a) shows that B3LYP results for two- and three-body, irrespective of the integration grid size, are close to corresponding MP2 results. In the case of four-body contributions, the significant difference between B3LYP-default (7.5%) and MP2 (3.3%) methods was observed. The B3LYP-default result has been improved to 4.2% on changing the integration grid size, i.e., UF (and/or SF). By changing the integration grids from default to UF to SF for B3LYP methods, the magnitude of five-body contribution has also been improved from 13.2% to 3.6% to 3.6% in comparisons with HF (2.8%) and MP2 (3.6%) results. In conjunction with higher integration grids, improvement of B3LYP results, particularly for four- and five-body contributions, was also observed in the case of BSSE-corrected values (Figure 1(b)). In the case of BSSE-corrected results, irrespective of the methods, we have observed that the five-body contribution is very small (less than 1%) which is in agreement with earlier literature.[18,21,22]

Thus, it is clear that MBE is susceptible to the numerical accuracy of subsystems calculations and more stringent convergence criteria may be useful. However, it is also observed that due to the combinatorial nature of MBE, the errors are amplifying (Table S1, S3 and S4 in SI). For instance, the difference between default and UF for $\sum E\,(i, j, k, l, m)$ value is $-4.86$ kcal/mol (Table S4 in SI) but the same difference for five-body term (i.e., $\Delta^5 E$) is 19.31 kcal/mol (Table S1 in SI) at B3LYP/6-311+G* level of theory in the case of $(H_2O)_{15}$. Note that the five-body term not only contains $\sum E\,(i, j, k, l, m)$, it also accommodates one-body ($E\,(i)$), two-body ($\Delta^2 E$), three-body ($\Delta^3 E$) and four-body ($\Delta^4 E$) terms. Therefore, the errors in smaller body terms are also introduced in five-body (i.e., $\Delta^5 E$) term. Moreover, the smaller terms (i.e., one- to four-body) in $\Delta^5 E$ multiply with a constant value (i.e., 1001, 286, 66 and 11, respectively), due to which the five-body term becomes more erroneous (see equation 6). Almost four-fold enhancements have also been observed in the cases of two-, three- and four-body energy terms at B3LYP level. These dramatic enhancements of the errors in $x$-body terms are mainly due to the combinatorial nature of MBE approach.

## 4. Conclusions

In the current study, many-body expansion (MBE) calculations have been carried out to investigate the two-to five-body energy terms and their contribution to the interaction energy of $(H_2O)_{15}$ cluster at MP2, HF and B3LYP level of theory with 6-311+G* basis set. We have observed that the erroneous contribution of many-body terms on IE originated from cheaper convergence thresholds set as default, especially in single-point calculation, in popular quantum mechanics packages. During the course of this study, we have found that the influence of SCF convergence criteria on IE and $x$-body ($x = 2$–5) energy terms at MP2 level seem to be small. However, these small variations of IE and $x$-body energy values with convergence criteria have almost no effect on the percentage contribution of $x$-body terms, but it indicates that because of the combinatorial nature of MBE, the error systematically propagated from two- to five-body terms. Although it was mentioned earlier that HF method is not adequate for MBE,[21,61] nevertheless, this method is less vulnerable to convergence criteria as observed in our study. The incorrect B3LYP results for four- and five-body energy terms of $(H_2O)_{15}$ can be improved with changing integration grid sizes from default to UF to SF. These incorrect B3LYP results clearly unveil the fact that MBE is susceptible to low sensitivity problems, as already mentioned in the literature.[62,63] Moreover, due to the combinatorial nature of MBE, the error is propagating from two- to five-body terms and these accumulated errors lead to the spurious error for higher body terms or may even become problematic to calculate for large systems, as MBE is a combinatorial function of both truncation order ($x$) as well as cluster size ($n$). Therefore, the most obvious next step is to explore the variation of cluster size ($n$) with $x$-body terms; currently, we are working on this direction. Although, the inclusion of higher-body terms (three-body onwards) will help in developing various methodological approaches for water; its inclusion may, however, produce erroneous results. Nevertheless, the results from our study will thrust to develop new approaches for water, which can be used in the modelling of a wide range of important chemical and biological systems.

## Supplementary Information (SI)

The full citation for Gaussian 09, Table for percentage contribution, Figure of $(H_2O)_{15}$ and optimized XYZ-coordinates of $(H_2O)_{15}$ are given in Supplementary Information which is available at www.ias.ac.in/ chemsci.

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