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Facilitating Minima Search for Large Water Clusters at the MP2 Level via Molecular Tailoring

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S *Supporting Information*

(H₂O)₂₀   (H₂O)₂₅   (H₂O)₃₀
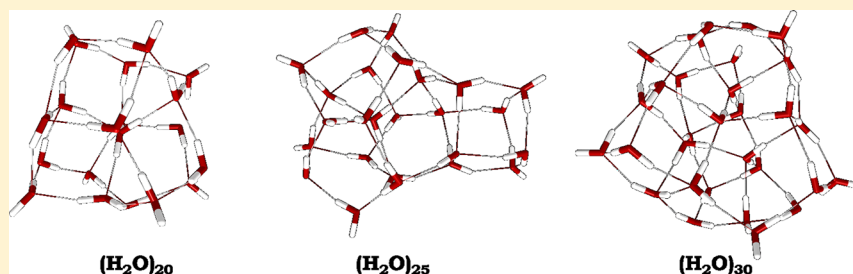
ABSTRACT: Water clusters $(H_2O)_{20}$ and $(H_2O)_{25}$ are explored at the Møller–Plesset second-order perturbation (MP2) level of theory. Geometry optimization is carried out on favorable structures, initially generated by the temperature basin paving (TBP) method, utilizing the fragment-based molecular tailoring approach (MTA). MTA-based stabilization energies at the complete basis set limit are accurately estimated by grafting the energy correction using a smaller basis set. For prototypical cases, the minima are established via MTA-based vibrational frequency calculations at the MP2/aug-cc-pVDZ level. The potential of MTA in tackling large clusters is further demonstrated by performing geometry optimization at MP2/aug-cc-pVDZ starting with the global minimum of $(H_2O)_{30}$ reported by Monte Carlo (MC) and molecular dynamics (MD) investigations. The present study brings out the efficacy of MTA in performing computationally expensive ab initio calculations with minimal off-the-shelf hardware without significant loss of accuracy.

SECTION: Molecular Structure, Quantum Chemistry, and General Theory

For its abundance on the surface of the Earth, the chemistry of water is rather poorly understood. Despite the numerous studies on the anomalies of water,[1,2] a complete picture at the molecular level is still being sketched and resketched. For instance, the study by Wernet et al.[3] challenged the conventional view that liquid water is a tetrahedrally coordinated network as seen in molecular dynamics (MD) simulations. Instead, it was suggested that a majority of the molecules have only two strong hydrogen bonds. Thus, the existing knowledge provides a strong hint that there is still a need for conclusive theoretical investigations on larger water clusters.

To understand the nature of water clusters, several Monte Carlo (MC)- and MD-based studies[4−18] have been performed for developing potentials for water and in search of minima on the corresponding potential energy surfaces. These studies lead to identifying well-characterized families of favorable hydrogen bonded networks. However, empirical many-body interaction potentials are not consistent in providing reliable energetics and rank ordering for larger clusters. Thus, ab initio calculations are vital not only for benchmarking the energetics of these potentials but also to accurately compute molecular properties such as polarizabilities and vibrational spectra.

Many landmark ab initio studies have been performed[19−24] on water clusters up to size $n = 25$ at the Hartree−Fock (HF) level of theory. In recent years, the advent of highly parallelizable software and computer hardware have enabled such studies at better correlated methods such as MP2, CCSD(T), and so forth.[25−34] However, these methods are very demanding in terms of computational resources as well as time. For example, Fanourgakis et al.[30] carried out a large calculation of single-point energy on $(H_2O)_{20}$ at MP2/aug-cc-pVQZ on hardware consisting of 512 Intel Itanium processors (1.5 GHz). For various low-lying isomers of $(H_2O)_{16}$ and $(H_2O)_{17}$, by computing single point energies at CCSD(T)/aug-cc-pVTZ, Yoo et al.[33] showed the relative reordering of energies at the CCSD(T) level of theory as compared to those at MP2. For $n = 16$, a typical wall clock time of 3.33 h for a single point CCSD(T) calculation was reported using as many as 120 000 cores. MP2 is the least expensive one among the post-HF methods, and calculations employing Dunning's correlation

consistent basis sets (such as aug-cc-pVXZ, X = D, T) have become a *de facto* standard for theoretical studies.

It is to be emphasized that for large water clusters, the number of nearly iso-energetic isomers is enormous.[35] Performing accurate ab initio calculations conventionally on all of these structures is a formidable task. Yet, omitting structures based on crude energetics increases the possibility of ruling out some energetically favorable ones.

The current study aims to efficiently search and investigate the structures and energetics of $(H_2O)_n$, $n = 20$ and 25 at the MP2 level of theory. The main hurdles in this study are (i) how to generate energetically favorable initial structures and (ii) how to minimize computational requirements for their ab initio treatment. The present work makes combined use of temperature basin paving (TBP)[18] and molecular tailoring approach (MTA)[36−40] overcoming these problems. This resulted in several local minima for $(H_2O)_{25}$ as well as an energetically favorable structure of $(H_2O)_{20}$ overlooked in many extensive investigations of $n = 20$.

Shanker et al.[18] have established the application and efficiency of the MC-based TBP method for finding a large number of low-energy minima of water clusters of size 20 and 25. This method is a modification of the well-known basin-hopping method.[41,42] Geometry optimization of these clusters at the MP2/aug-cc-pVDZ level of theory is demanding in terms of computational resources as well as time. Thus, an efficient fragment-based method MTA is employed to accelerate the process. MTA is a divide-and-conquer (DC) technique in which the large molecular system is broken into a set of overlapping fragments, on which ab initio calculations are performed. The required results, i.e., energy, gradients, and so forth, are reconstructed from the fragments to estimate those for the main molecule. MTA-Plug-In,[43] a software that automates the procedure outlined above, is utilized in the calculations. Fragment size and number of fragments were varied according to the size of the cluster so as to always provide a noticeable time advantage over a conventional calculation of the same type. The details of algorithm, fragmentation, and control parameters used in MTA are given elsewhere.[38,43] All the fragments and images are created with the package MeTA Studio.[44]

Treating water clusters by fragment-based methods is always challenging, due to the compactness of their structures, randomness in the orientation and the strong co-operative dipolar effects. Thus, water clusters when treated with fragment-based strategies may produce erroneous energy estimates. However, it has been shown[39] that the errors in MTA-based energy estimates are generally independent of the basis set employed. In other words, for a particular fragmentation scheme, the error in MTA-energy remains nearly constant regardless of the basis set used. It is also noticed that at the MP2 level, the major contribution in the gross MTA-based error in energy comes[39,45] from the error in HF rather than the second-order perturbative correction, i.e., $E(2)$. These facts can be utilized for achieving accurate MTA-energy estimates by "grafting" the MTA-error in $E(2)$ at the "lower" basis set as a correction to the MTA-energy at the desired "higher" basis set. The lower basis set is chosen such that it is comparable in terms of the quality to the higher basis set and is also relatively computationally inexpensive for calculations. The grafting method is proposed as follows:

1. Evaluate $E(HF)_{Actual/HB}$, the actual single-point energy at HF level with the desired higher basis set (HB).

2. Perform MTA-based single-point energy calculation and obtain $E(2)_{MTA/HB}$, the cardinality-based second-order perturbative correction.

3. Determine correction $\delta E(2)_{LB}$ at a suitable lower basis set (LB) to be grafted on to $E(2)_{MTA/HB}$ as

$$\delta E(2)_{LB} = E(2)_{Actual/LB} - E(2)_{MTA/LB} \qquad (1)$$

4. Accurate MTA-based second-order perturbative correction, $E(2)_{MTA/HB}^{Corr}$, at the desired higher basis set is obtained (eq 2), and the final MTA-based energy estimate $E(MP2)_{MTA/HB}$ at the higher basis set is determined (eq 3).

$$E(2)_{MTA/HB}^{Corr} = E(2)_{MTA/HB} + \delta E(2)_{LB} \qquad (2)$$

$$E(MP2)_{MTA/HB} = E(HF)_{Actual/HB} + E(2)_{MTA/HB}^{Corr} \qquad (3)$$

It is noteworthy that the actual energy calculation at the HF level is computationally inexpensive, and if used in MTA-based estimates, it would eliminate the larger component error completely. After much consideration and testing, it is seen that 6-31+G** is the best-suited basis set as the LB to graft the correction in aug-cc-pVDZ (HB). On similar lines, for aug-cc-pVTZ as HB, aug-cc-pVDZ is used as the LB. These are employed for determining the stabilization energies for all the final optimized geometries of $(H_2O)_{20}$ and $(H_2O)_{25}$ structures. Subsequently, the two-point formula proposed[46] by Helgaker and co-workers is applied to estimate the stabilization energies of these clusters at the complete basis set limit.

$$\Delta E_{CBS(DT)} = [27\Delta E_{TZ} - 8\Delta E_{DZ}]/19 \qquad (4)$$

where ΔE_{XZ}, X = D, T, stands for stabilization energy of a cluster with an aug-cc-pVXZ basis set.

In summary, the structures generated by the TBP method are broadly filtered based on the effective fragment potential (EFP), a polarizable water potential.[47] Six unique low-energy structures of $(H_2O)_{20}$ are subjected to MTA-based geometry optimization at MP2/6-31+G** and further at the MP2/aug-cc-pVDZ level of theory. However, in the case of $(H_2O)_{25}$, the energetically lowest six structures out of 12 MTA-optimized structures at MP2/6-31+G** are chosen for further optimization at MP2/aug-cc-pVDZ. Further single-point energy calculations are performed via MTA at MP2/aug-cc-pVTZ. All the ab initio calculations are performed using the Plug-In[43] version of MTA with the Gaussian 09 package[48] and the NWChem 6.1 suite of programs[49] as the backend. All the calculations are performed on a maximum of four Intel Core i7 CPUs @ 2.93 GHz with 16 GB RAM each. On two of these desktop machines, an MTA-based single point energy-gradient calculation at MP2/aug-cc-pVDZ typically takes wall clock times of 210 and 600 min for $(H_2O)_{20}$ and $(H_2O)_{25}$, respectively. The large calculations, i.e., MTA-based Hessian and the actual single-point energies are performed using a maximum of eight nodes of the National Param Super-computing Facility, Center for Development of Advanced Computing, Pune.

The MTA-based energies for the optimized geometries for $(H_2O)_{20}$ and $(H_2O)_{25}$ are seen to be in error by a few milliHartrees (2−10 mH) with reference to the respective actual energies. Therefore, these are improved by grafting the correction that is calculated at the lower basis as above (cf. eqs 1, 2, and 3). These grafted MTA-based energies (Tables 1 and 2) are in error by 0.01 to 0.3 mH for $(H_2O)_{20}$, which are seen to grow from 0.35 to 0.71 mH $(H_2O)_{25}$ at MP2/aug-cc-pVDZ.

Table 1. MTA-Based Final Energies, $E(MP2)_{MTA/HB}$ (in H), for $(H_2O)_{20}$ and $(H_2O)_{25}$ at the MP2/aug-cc-pVDZ Level of Theory According to Eqs 1, 2 and 3^a

system	$E(HF)_{Actual/HB}$	$E(2)_{MTA/HB}$	$\delta E(2)_{LB}$	$E(MP2)_{MTA/HB}$	ε
20-A	−1521.03037	−4.54197	−0.00034	−1525.57266	0.11
20-B	−1521.03433	−4.53853	−0.00032	−1525.57291	0.10
20-C	−1521.03046	−4.54147	−0.00042	−1525.57235	0.03
20-D	−1521.02796	−4.54124	−0.00012	−1525.56931	0.06
20-E	−1521.03230	−4.54235	−0.00054	−1525.57519	0.07
20-F	−1521.03269	−4.53801	−0.00019	−1525.57088	0.31
25-A	−1901.29293	−5.68880	−0.00072	−1906.98245	0.35
25-B	−1901.29901	−5.68157	−0.00039	−1906.98097	0.50
25-C	−1901.29226	−5.68715	−0.00097	−1906.98038	0.71
25-D	−1901.30352	−5.67685	−0.00026	−1906.98064	0.25
25-E	−1901.29601	−5.68458	−0.00039	−1906.98098	0.32
25-F	−1901.29537	−5.68281	−0.00051	−1906.97869	0.65

^{a}The errors, ε (mH), in MTA energies are calculated with reference to respective actual energies (cf. the table in the Supporting Information). LB and HB stand for 6-31+G** and aug-cc-pVDZ, respectively.

Table 2. MTA-Based Final Energies, $E(MP2)_{MTA/HB}$ (in H), for $(H_2O)_{20}$ and $(H_2O)_{25}$ at the MP2/aug-cc-pVTZ Level of Theory According to Eqs 1, 2, and 3^a

system	$E(HF)_{Actual/HB}$	$E(2)_{MTA/HB}$	$\delta E(2)_{LB}$	$E(MP2)_{MTA/HB}$
20-A	−1521.39840	−5.52824	−0.00046	−1526.92671
20-B	−1521.40132	−5.52374	−0.00018	−1526.92590
20-C	−1521.39732	−5.52898	−0.00040	−1526.92638
20-D	−1521.39490	−5.52880	−0.00027	−1526.92367
20-E	−1521.39920	−5.52973	−0.00060	−1526.92956
20-F	−1521.39953	−5.52537	−0.00049	−1526.92539
25-A	−1901.75050	−6.92250	−0.00107	−1908.67300
25-B	−1901.75691	−6.91453	−0.00088	−1908.67232
25-C	−1901.75061	−6.91977	−0.00168	−1908.67206
25-D	−1901.76167	−6.90973	−0.00051	−1908.67191
25-E	−1901.75385	−6.91728	−0.00071	−1908.67183
25-F	−1901.75307	−6.91594	−0.00116	−1908.67017

^{a}LB and HB stand for aug-cc-pVDZ and aug-cc-pVTZ, respectively.

However, it may be pointed out that fragments of comparable size are employed for both the clusters, and the error for $(H_2O)_{25}$ can be reduced by enhancing the corresponding fragment size marginally. It is evident that at the respective basis set, the rank ordering of the grafted MTA-based energetics is always maintained within the resolution of ∼0.2 mH as compared to their actual counterparts (Tables 1 and 2). Unfortunately, due to lack of sufficient hardware, actual calculations at MP2/aug-cc-pVTZ were not possible for comparison. These grafted MTA-based energies are used for determining the stabilization energies at the CBS limit as shown in Table 3.

According to the present study, among the six structures of $(H_2O)_{20}$ (cf. Figure 1), 20-E emerges as the most stable one. The structure of 20-E consists of edge-sharing pentagonal prisms, and this is in agreement with the global minimum of $(H_2O)_{20}$ found at *ab initio*[30,34] as well as MD studies[10] reported in the literature. A surprising feature is a quite stable, "internally solvated" type structure, viz., 20-B, not noticed hitherto in the literature for $(H_2O)_{20}$. It consists of a fully coordinated water molecule at the center surrounded by 19 other molecules forming an "internally solvated" structure. The minimum for this type of water cluster was reported for $(H_2O)_{17}$ by Yoo et

Table 3. MTA-Based Stabilization Energies for $(H_2O)_{20}$ and $(H_2O)_{25}$ at the MP2 with aug-cc-pVDZ (DZ), aug-cc-pVTZ (TZ), and CBS Limit in kcal/mol^a

system	$\Delta E(MP2)_{MTA/DZ}$	$\Delta E(MP2)_{MTA/TZ}$	$\Delta E(MP2)_{MTA/CBS}$
20-A	−222.4	−218.4	−217.7
20-B	−222.6	−217.7	−215.6
20-C	−222.2	−218.1	−216.4
20-D	−220.3	−216.2	−214.5
20-E	−224.0	−219.9	−218.2
20-F	−221.3	−217.3	−215.7
25-A	−288.5	−281.9	−279.1
25-B	−287.5	−281.4	−278.9
25-C	−287.2	−281.3	−278.8
25-D	−287.3	−281.2	−278.6
25-E	−287.5	−281.1	−278.4
25-F	−286.1	−280.1	−277.6

^{a}Stabilization energies computed using the following energies for water monomer (in H): $E(MP2/aug\text{-}cc\text{-}pVDZ//MP2/aug\text{-}cc\text{-}pVDZ)$ = −76.26091; $E(MP2/aug\text{-}cc\text{-}pVDZ//MP2/aug\text{-}cc\ pVTZ)$ = −76.32895.

al.[33] representing a transition from an "all-surface" to "internally-solvated" type of structure with increasing n. The other structures 20-A, 20-C, 20-D, and 20-F are of "all-surface" type and consist of different arrangements of pentagonal prisms and fused cubes. It is also noted that after complete MTA-based geometry optimization at MP2/aug-cc-pVDZ, the hydrogen bonding networks as well as the cage-like arrangements are generally preserved.

For the case of $n = 25$, the most stable structure, viz., 25-A, is different than the minimum reported in the literature.[15,16,34] As evident from Figure 2, 25-A has a "internally solvated" $(H_2O)_{21}$ cluster and a cyclic tetramer attached to the side. Structures 25-B, 25-E, 25-D, and 25-F have a nearly consistent oxygen-framework consisting of three adjacent pentagonal prisms distorted by the "intrusion" of additional monomers. These resemble the lowest minimum found so far.[15,16,34] On the other hand, structure 25-C ranks third in stability and is characterized by a complete $(H_2O)_{24}$ cage comprising cyclic tetramers, pentamers, and hexamers with a water monomer in the center. Even though the basic frameworks of the structures differ, the spread in energies is only 1.5 kcal/mol.

A point to note is the complete change in rank ordering if only the HF-energetics are considered (cf. Tables 1 and 2). A comparison shows that the contribution from the second-order perturbation correction is large enough to override that of HF, emphasizing the need for optimization at the MP2 level.

It is seen that the hydrogen bonding network of 20-E is identical to the edge-sharing global minimum reported by Fanourgakis et al.[30] at the MP2/aug-cc-pVDZ level of theory. The raw energy for this structure is reported[30] as −1525.57601 au, while the grafted MTA-based energy corresponding to the similar edge-sharing structure 20-E is −1525.57519 au, which is 0.8 mH higher. The convergence criterion for MTA-based geometry optimization on maximum and rms gradients is 10^{-4} a.u., but owing to the approximate nature of MTA, the final MTA-optimized structure may not be fine-tuned. Thus, in order to ensure a refined structure, 20-E is further optimized with larger fragments to better represent the gradients. This brought the MTA-based energy of 20-E to be −1525.57583 on grafting, just 0.17 mH higher in energy compared to the global minimum by Fanourgakis et al.[30] The initial fragmentation
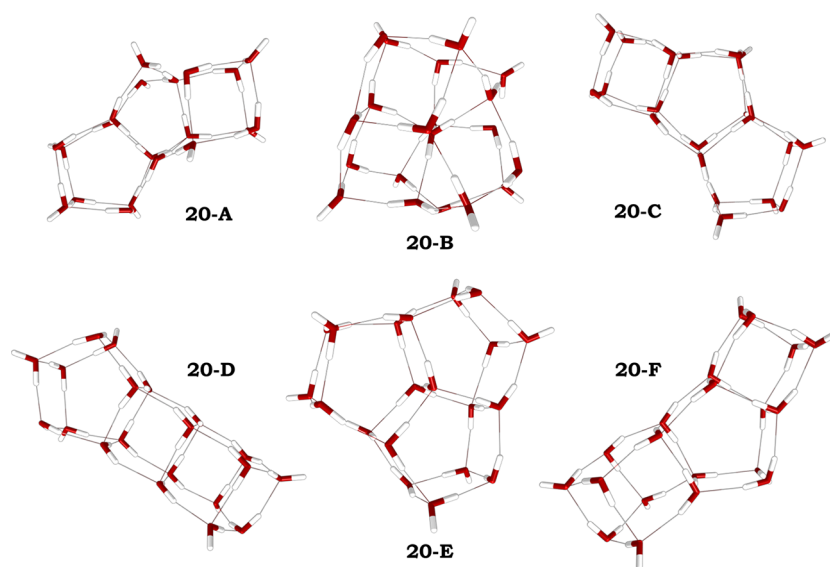
Figure 1. Final MTA-optimized geometries of the $(H_2O)_{20}$ clusters considered in the present study at the MP2/aug-cc-pVDZ level of theory.

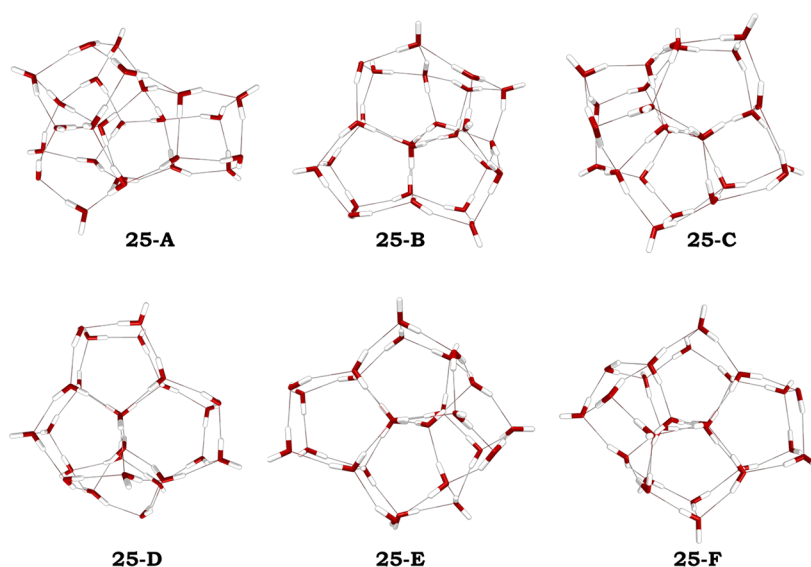**Figure 2.** Final MTA-optimized geometries of the $(H_2O)_{25}$ clusters considered in the present study at the MP2/aug-cc-pVDZ level of theory.

scheme for 20-E consists of 11 main fragments that have an average size of nine water molecules, while for further fine-tuning, nine main fragments with an average size of 12 water molecules are employed. With similar sets of fragments, 20-B is also subjected to further optimization owing to the uniqueness of the structure, and the grafted MTA-based energy at the MP2/aug-cc-pVDZ is seen to come down to −1525.57387 au. This is seen to be lower than fused-cubes, face-sharing, and dodecahedron families of $(H_2O)_{20}$ reported[30] in the literature.

It has been noticed previously that even if the MTA-based energies are in error by a few milliHartrees, the gradients are accurate enough, and the MTA-based geometry optimization generally leads to the local minimum structure. In view of this, MTA-based Hessian calculations are performed on two of the final optimized geometries of $(H_2O)_{20}$, viz., 20-B and 20-E, at the MP2/aug-cc-pVDZ level of theory, and one of $(H_2O)_{25}$, viz., 20-D. In all the cases, the MTA-based Hessian matrix gives all the real frequencies, confirming the local minimum nature of the structure.

As a further demonstration of the capability and scope of MTA, the global minimum for $(H_2O)_{30}$ as reported by Kazachenko et al.[16] is taken up as a starting structure for geometry optimization at the MP2/aug-cc-pVDZ level of theory. A computationally feasible fragmentation scheme of a total of 22 main fragments of an average size of 32 atoms is employed. The complete MTA-based geometry optimization (final geometry depicted in Figure 3) took a total wall clock time of 16 days on the hardware of four Intel Core i7 CPUs @ 2.93 GHz with 16 GB RAM each. This calculation shows the utility of MTA to enable such a computationally expensive run on merely four desktop machines. The grafted MTA-based stabilization energy for the final optimized geometry is found to be −351.8 kcal/mol at MP2/aug-cc-pVDZ level of theory. It may be noted that at the optimized geometry, the hydrogen bond lengths range from 1.66 to 2.01 Å, of which 22 out of 52 hydrogen bonds lie between 1.66 to 1.8 Å.

In summary, the present work has illustrated how to generate energetically favorable structures of $(H_2O)_{20}$ and $(H_2O)_{25}$ via

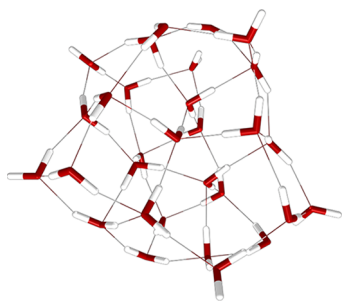**Figure 3.** $(H_2O)_{30}$ optimized at the MP2/aug-cc-pVDZ level of theory.

combined use of TBP and MTA methods. The TBP method is applied to search potentially low-energy initial structures, which are further investigated at the MP2 level of theory with MTA. There is a need to employ MTA to decrease the huge computational demands of MP2 and enable such calculations on off-the-shelf hardware. Apart from minimizing resources, use of MTA also achieves substantial time saving, especially in the case of geometry optimization at the MP2/aug-cc- pVDZ level. The method of grafting correction from lower basis set improves the MTA-based energies, successfully bringing down the errors from a few kcal/mol to well within ~0.5 kcal/mol, for all the cases examined in this study. Since the level of theory is no bar, it would be worthwhile extending the present methodology to the "gold standard" of contemporary quantum chemistry, viz., CCSD(T)/CBS. It is hoped that the encouraging results of the present study pave the way for taking up investigations on water clusters containing 100 monomers at the ab initio level of theory in the near future.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information
Detailed tables on grafting as well as MP2/aug-cc-pVDZ optimized geometries for $(H_2O)_{20}$ and $(H_2O)_{25}$ are provided in the Supporting Information. 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.

■ ACKNOWLEDGMENTS

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