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Unraveling Hydrogen Bonded Clustering with Water: Density Functional Theory Perspective

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Abstract

Extensive density functional theory (DFT) studies have been compiled and additional investigation has been performed for several energetically favorable conformers of hydrogen bonded water clusters. The focus here is not to merely reviewing the literature on DFT investigations on water clusters but to understand the basic building blocks, structural patterns and trends in the energetics of the clusters during the cluster growth. The successive addition of water molecules to these clusters alters the hydrogen bonding pattern, that leads to modification in overall cluster geometry which is also reflected in the vibrational frequency shifts in simulated vibrational infra-red (IR) spectra.

Keywords: hydrogen bonding, water clusters, ab initio, quantum chemistry, density functional theory

1. Introduction

Water is the most ubiquitous substance on this planet and has probably received more scientific and technological attention than any other substance. *Water clusters*, in particular, the groups of water molecules held together by hydrogen bonds, have been the subject of a number of intense experimental and theoretical investigations for the past century due to their importance in chemistry [1], atmospheric chemistry [2], understanding cloud and ice formation, as well as a large number of physico-chemical and biochemical processes [3]. The exploration of the structural and binding properties of water clusters is the first step to understand the properties of bulk water, the essence of life. The difficulty in obtaining a rigorous molecular scale description of the structure of liquid and solid water is mainly due to the constantly fluctuating hydrogen-bonding network therein. This cooperative hydrogen-bonding in water molecules gives rise to the fascinating arrays of anomalous properties. Also, the cooperativity in aggregates of water molecules is particularly important towards understanding the behavior of the liquid and ionic as well as molecular hydration.

A look at the available literature reveals several monographs as well as reviews [4–9] providing detailed understanding of structures as well as binding, spectral and chemical properties of water and its related clusters. The following discussion comprises a brief review of earlier benchmarking studies on water clusters with a special reference to the structure, energetics and the spectra.

Almost six decades ago, Clementi and co-workers [10] performed benchmarking studies on the water clusters, $(H_2O)_n$, n = 2–8 within Hartree-Fock

(HF) framework. The water dimer, the smallest member of the water cluster family has been studied extensively within experimental [11–13] as well as theoretical framework [9, 14–17] ($\Delta E = 5.5 \pm 0.7$ kcal.mol^{-1} and C_s symmetry) since it forms a classical case of hydrogen bond.

According to several experimental [18–22] as well as theoretical studies, the energetically most favorable structure of the water trimer has been confirmed to be cyclic with C1 symmetry. This structure has one external hydrogen atoms on one side of the O-O-O plane and two hydrogen bonds on the other side of the plane. Also, each monomer in this case behaves as a donor as well as an acceptor. Several *ab initio* quantum chemical investigations [4, 6, 7, 14–16, 23–27] have advocated a cyclic, homodromic structure with S_4 symmetry of Water tetramer, $(H_2O)_4$ which corresponds to the global minimum. The cyclic water tetramer has the free hydrogen atoms in alternate fashion above and below the plane of the O-O-O-O ring. This structure has also been observed in IR-studies of benzene-$(H_2O)_4$ and VRT spectra of $(D_2O)_4$ and $(H_2O)_4$ [28, 29]. Pentagonal rings of $(H_2O)_5$ are quite common in clathrate hydrates and in the solvation of hydrophobic groups of small molecules as well as in proteins and in DNA molecules.

Interestingly, the most stable structure for the pentamer follows the puckered cyclic ring pattern [1, 14, 30–32] whereas the *ab initio* studies [4, 6, 15, 16, 23–27] also predicted such a ring structure. Wales [33] pointed out the existence of different ring structures that can be interconverted through low energy barrier pathways consisting of the flipping of hydrogen atoms and bifurcation mechanisms.

The hexamer of water, $(H_2O)_6$ shows a transition from cyclic to three-dimensional geometries, and could be yet another cluster which has been studied extensively by theory [4, 6, 15, 16, 24–27, 34] and experiments [22, 35, 36]. Several studies [4, 6, 15, 16, 22, 24–27, 34–36] have demonstrated that a large number of alternative three-dimensional structures, such as chair, boat, book, jaws, ring and cage, are likely to be of comparable energies. The study of $C_6H_6 \ldots (H_2O)_6$ by Pribble and Zwier [35] could be considered as the first experimental evidence for the cage structure. Later on, Liu *et al*. [36, 37] also have verified the cage structure of isolated water hexamer through their FIR-VRT spectroscopy. Zero-point vibrational energy (ZPE) seems to play an important role in deciding the preferred geometry of the hexamer. In a recent studies due to Bates and Tshumper [38] proposed that the prism structure is marginally by 0.06 kcal.mol-1 and 0.25 kcal.mol^{-1} at MP2/CBS and CCSD(T)/CBS corrected for zero-point vibrational energy (ZPE) respectively.

Size-specific IR spectra of benzene-$(H_2O)_7$ clusters [35] suggest a compact noncyclic structure for $(H_2O)_7$ whereas IR-UV and UV–UV double resonance spectra of jet-cooled phenol-$(H_2O)_7$ clusters supported a cuboid structure for the heptamer, with one corner being occupied by the phenolic oxygen atom [39]. The vibrational spectrum of pure $(H_2O)_7$ [40] indicate the existence of two isomers derived from the S_4 octamer cube by the removal of either a double-donor or a double-acceptor water molecule.

Extensive *ab initio* calculations [4, 10, 16, 41–47] suggest that, at low temperatures, $(H_2O)_8$ would stabilize into a cube with D_{2d} or S_4 symmetry and that, at higher temperatures, entropy considerations could favor the other geometries. Experiments involving pure water clusters [48] as well as hydrated molecules, such as and phenol-$(H_2O)_8$, [39] and C_6H_6-$(H_2O)_8$ [49] also support the cubic structure of $(H_2O)_8$. Maeda and Ohno [30] explored 164 local minima of $(H_2O)_8$ employing MP2/6-311++G(3df,2p)//B3LYP/6-311 + G** level. They have observed that the D_{2d} isomer was energetically most stable than the S_4 isomer of $(H_2O)_8$. Thus, it may be seen that the smaller water clusters, $(H_2O)_n$, n < 8 have been subject of intense investigation within theoretical framework.

Several possible conformers of various water clusters, $(H_2O)_n$, up to nonamer were explored employing continuum solvation model by Malloum and Conradie [31]. They used MN15 DFT framework [32] with 6-31++G(d,p) basis set. According to this study the structures of $(H_2O)_n$ in continuum solvation (IEF-PCM) framework qualitatively similar to their gas phase counterpart. However, the hydrogen bonds show elongation in continuum solvent. The authors also suggested the effectiveness of MN15/6-31++G(d,p) density functional theory model chemistry for studying water clusters Jensen *et al*. [50] explored 44 possible structures of water nonamer using extensive HF calculations using the 6-311G(d) and 6-311G(d,p) basis sets. It was observed that the energetically favorable structure of water nonamer consist of stacked pair of cyclic water tetramer and pentamer which could be thought of as an extended cube. The computational predictions are in qualitative agreement with the available experimental result [51].

About a decade ago, Shields and coworkers [52] performed a detailed investigations on $(H_2O)_n$, n = 2–10; employing a combined molecular dynamics and quantum mechanical framework. The focus of the work was on the structures and energetics of water heptamer, nonamer and decamer structures. They observed that the 30 conformers of $(H_2O)_{10}$ spanned within the short range of 2 kcal.mol^{-1} of Gibb's free energy computed at 298 K. They used least-squares fitting based extrapolation and a new approach (MP2/CBS-e) incorporating counterpoise (CP) correction to basis set superposition error. The O-H stretch spectra [51, 53] of $(H_2O)_{10}$ seem to support a butterfly structure and not a fused cage.

For larger clusters viz. $(H_2O)_n$, n > 8 there exist some notable computational studies [4–6, 8, 16, 31, 54–59] with employing different levels of theory including the Gold-Standard CCSD(T) level of theory in conjugation with complete basis set (CBS) extrapolation for some structurally important prototype clusters. Todorova and coworkers on the basis of a detailed study involving modified B3LYP, X3LYP, and PBE0 functionals concluded that the modified functionals show better agreement with the experimental structures (in terms of radial distribution function) and dynamics (in terms of self-diffusion constant) properties of liquid water.

Lee and coworkers [60] studied $(H_2O)_{11}$ (undecamer) and $(H_2O)_{12}$ (dodecamer) employing Møller–Plesset second order perturbation theory (MP$_2$) with TZ$_2$P++ basis set. The undecamer structure is though as a combination of cyclic $(H_2O)_5$ and $(H_2O)_6$ with 16 hydrogen bonds. Similar structure for $(H_2O)_{11}$ has been confirmed by Bulusu *et al*. [61] in their study at B3LYP/6-311+G(d,p) level. They also extended their study for $(H_2O)_{13}$. In case of $(H_2O)_{12}$, the isomer arising from stacking of three cyclic tetramers with 20 hydrogen bonds and patterns $(D_{2d})_2$ or $(D_{2d})(S_4)$ or $(S_4)_2$ are energetically favorable conformers [4, 46] on potential energy surface. There also exists another low-lying conformer comprising two fused hexameric units held together by 18 hydrogen bonds. The $(H_2O)_{13}$ structure as confirmed by Bulusu et al. [61] is composed of an addition of isolated water molecule to the $(H_2O)_{12}$ cluster with cuboid conformation.

CCSD(T) level study on dipole polarizability of water clusters upto $(H_2O)_{12}$ has been reported by Hammond *et al*. [62]. This study also involve performance assessment of six density functionals namely. PBE, PBE0, B3LYP, BLYP, X3LYP and PW91. The authors concluded that the density functional PBE0 with aug-cc-pVDZ yield better agreement with the results from CCSD(T) level of theory than the other density functionals.

In a benchmarking study, Bryantsev and coworkers [16] investigated some structurally important neutral and charged water clusters viz. $(H_2O)_n$, n = 2–8, and 20, $H_3O^+(H_2O)_n$, n = 1–6, and OH-$(H_2O)_n$, n = 1–6. They employed B3LYP, X3LYP, M06, M06-L and M06-2X density functionals as well as Møller-Plesset perturbation theory (MP2) and coupled-cluster theory with single, double, and perturbative

triple excitations CCSD(T) levels of theory with various extended basis sets. The basis sets employed were aug-cc-pVnZ, where n = 2, 3, 4 and 5. It was concluded that Minnesota density functionals namely M06 and M06-L used with aug-cc-pV5Z basis set yield vary small mean unsigned error (MUE) of $\sim$0.73–0.84 kcal.mol^{-1}. However, these methods are computationally very expensive even for medium-sized water clusters. In a detailed benchmarking investigation on $(H_2O)_{16}$ and $(H_2O)_{17}$, Leverentz and coworkers [54] employed 61 levels of density functionals, 12 computational methods combining DFT with molecular mechanics (MM) damped dispersion (DF-MM), seven semiempirical methods, as well as semiempirical methods with MM- damped dispersion. The results from their study were compared with those from CCSD(T)/aug-cc-pVTZ level of theory [63]. They advocated that the density functionals viz. M06-2X, M05-2X, ωB97X-D, SCC-DFTB-g are good for binding energies.

A generalized energy-based fragmentation (GEBF) approach was used by Wang and Li [64] to compute the interaction energies of $(H_2O)_{20}$ conformers at explicitly correlated version of coupled-clusters with singles, doubles and triple excitation (CCSD(T)-F$_{12}$) level of theory. They have also computed interaction energies of these conformers using 32 different levels of DFT-framework. Based on the detailed investigation it was concluded that the functionals ωB97X-D and M05-2X functional show good agreement in absence of empirical dispersion correction. Also, the functionals including the empirical dispersion corrections viz. LC-ωPBE-D3 and B97-D show very close agreement with the CCSDT results. The same approach was employed by Yuan and coworkers [65] to investigate relative energies of large water clusters namely $(H_2O)_n$, n = 32, and 64.The energies computed with GEBF method were compared with CCSD(T) and MP2-levels of theories combined with CBS-limit. It was concluded that the popular functionals viz. B3LYP, PBE0, and DFTB3 do not yield accurate energies whereas the functionals viz. LC-ωPBE-D3 and ωB97X-D yield better agreement of relative energies when compared with CCSD (T)/CBS-level of theory. They advocated use of at-least aug-cc-pVTZ basis set for computational studies on water clusters as well as clusters in aqueous solutions.

Mallhoun *et al*. [8] on performed a careful study of $(H_2O)_n$, n = 2–30 employing the M06-2X functional with aug-cc-pVTZ basis set. They observed that the cage structures are energetically more dominating as compared to the stacked structures comprising tetrameric and pentameric units for $(H_2O)_n$, where n = 26–30. The computed relative energies of their study are in good agreement with the earlier results with CCSD(T)/CBS level of theory. On the basis of their results, it was concluded that performance of the density functional when compared with CCSD(T)/CBS in the increasing order is: MN15 [32], ωB97X-D, M06-2X and APFD. The density functional, MN15 from Truhlar and coworkers outperforms all other density functionals.

Thus, it may be seen from above discussion that a study comprising a short review of benchmarking studies on structures, and energetics of water clusters, $(H_2O)_n$ is warranted. The present work also involves an unbiased assessment of some well-known density functionals for small prototype water clusters, as well as the understanding of basic building blocks for building bigger clusters.

2. Computational methodology

2.1 Benchmarking of the DFT framework

In order to benchmark the density functionals, the present work involves use of two *ab initio* theories, namely Hartree-Fock (HF), Moller-Plesset second order perturbation theory (MP2) and eleven different density functionals, viz. B3LYP

[66–68], B3PW91, BHandHLyp, BLYP, PBE0, M06 [69, 70], M06-2X [69, 70], M06-L [69, 70], τ-HCTHHyb [71], ωB97X [72], AND ωB97X-D [73]. These methods were used in combination with a variety of basis sets viz. 6-31G(d,p), 6-311++G(d,p), 6-311++G(2d,2p), aug-cc-pVDZ, aug1-cc-pVTZ (aug-cc-pVTZ on Oxygen atoms and cc-pVTZ on Hydrogen atoms), aug-cc-pVTZ as well as def2-TZVP for benchmarking the density functionals. Thus, the benchmarking of smaller clusters was done with 91 different model chemistries against the Gold-standard method, coupled-cluster theory with singles, doubles and triples excitation (CCSD(T)/aug-cc-pVQZ). The water clusters, $(H_2O)_2$ and $(H_2O)_3$ and the isolated water molecules were selected for benchmarking the interaction energy and structural parameters.

2.2 Structure generation

The prototype structures viz. isolated water molecule, water dimer and trimer were selected for this benchmarking. The initial structures of the energetically favorable water clusters, $(H_2O)_n$ were taken from the earlier benchmarking studies which are based on the supermolecular approach [4, 14, 27, 62]. These structures were subjected to further geometry optimization within the judiciously shortlisted DFT-framework.

2.3 Computational framework

Initial optimization of all the structures at Hartree-Fock (HF), and Moller Plesset second order perturbation theory (MP2) level with computationally decent and manageable basis set, 6-31G(d,p) was performed employing Gaussian 09 [74] and GAMESS [75]. For standardization of the results, the geometry optimization, vibrational frequency computations were carried out using Gaussian 09 suite of program with default options. However, for all the density functional theory calculations the integration grid specified was an ultrafine pruned grid with 99 radial shells and 590 angular points per shell as defined in the Gaussian 09 suite [74].

3. Results and discussion

The present work embarks on providing an extensive overview of notable investigations on water clusters, $(H_2O)_n$ within quantum chemical as well as density functional theory framework. The results of present work are summarized below.

Selection of an appropriate computational framework which is also known as model chemistry (that is a combination of a computational theory and a basis set) for a given problem is an extremely tough task due to availability of wide range of methods and variety of basis sets. The same fact is evident in the Introduction section that outlines a wide range of computational methodologies including DFT framework employed for water clusters.

In order to understand the trends in energetics and structures, some structurally important prototype clusters, viz. $(H_2O)_n$, n = 1–6, 8, 20 were selected for which some data at high-levels of theory is available. Also, for benchmarking of density functionals the smaller clusters viz. $(H_2O)_2$, and $(H_2O)_3$ were studied employing 91 model chemistries (as mentioned in the Methodology Section) against the Gold-standard method, coupled-cluster theory with singles, doubles and triples excitation (CCSD(T)/aug-cc-pVTZ) [16]. The various $(H_2O)_n$ clusters considered for reviewing are depicted in **Figure 1**. The details of interaction energy data compiled from the present investigation as well as other notable studies is compiled in **Table 1**.
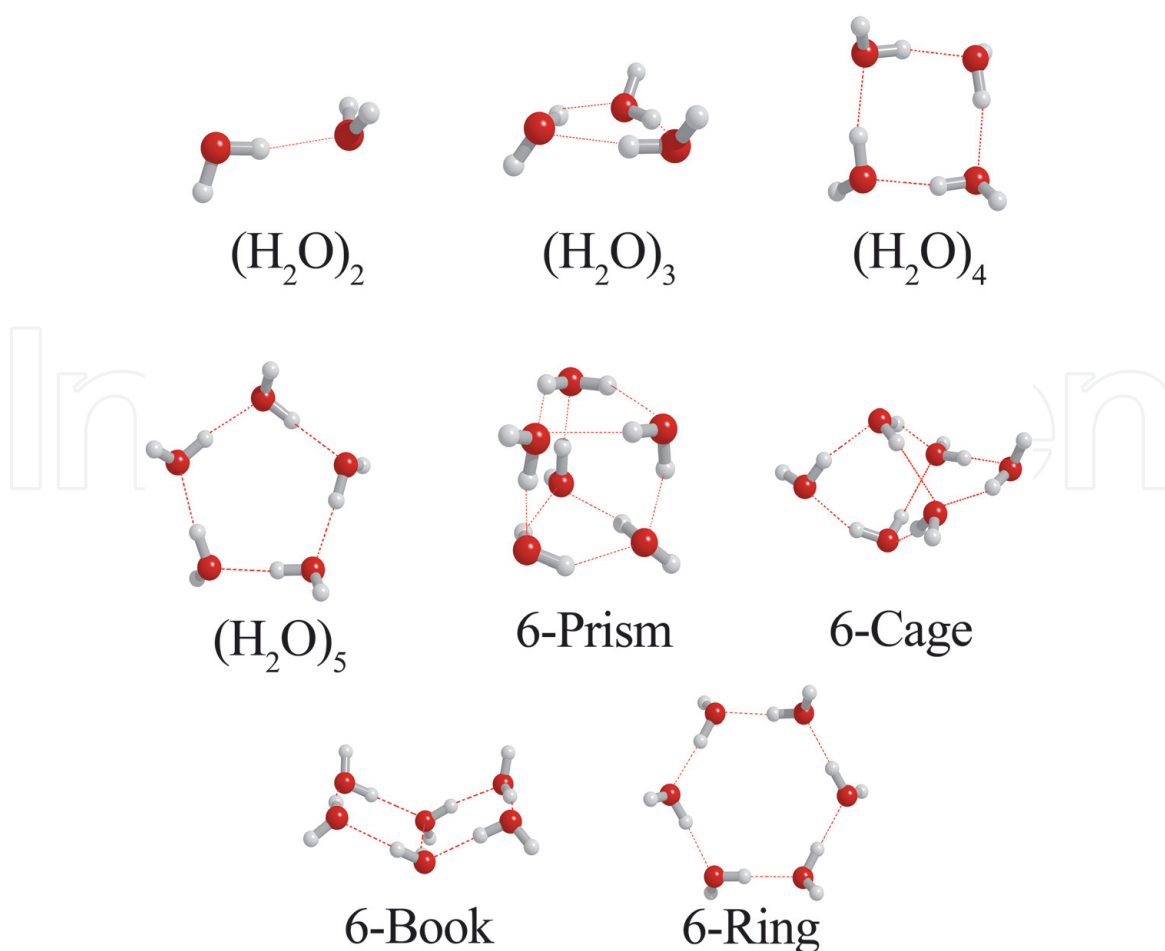
Figure 1.
Schematic representation of B3LYP/6-311++G(2d,2p) optimized structures of $(H_2O)_n$, n = 2–6. Data derived from ref. [16]. Oxygen atoms are denoted by Red spheres, Hydrogen atoms by White-Grey color. Dotted lines represent hydrogen bonds.

The mean unsigned errors for structural parameters viz. bond lengths, bond angle as well as energetics of $(H_2O)_2$ and $(H_2O)_3$ are presented in **Tables 2–4** respectively. The energies for larger clusters were adapted from other references as mentioned in the respective Tables. It may be seen from the **Table 1** that all the computational model chemistries involve an extensive aug-cc-pVTZ basis set that make use of 92 basis functions per water molecule. Thus, as an example studying a water clusters $(H_2O)_{30}$ would require 2760 basis functions, which makes the exploring and scanning of several energetically favorable conformers, rather an arduous task.

In order to explore a convenient alternative to a computationally demanding, aug-cc-pVTZ basis set, a truncated version of aug-cc-pVTZ basis set was employed which involve the use of aug-cc-pVTZ basis set on Oxygen atoms and cc-pVTZ basis set on Hydrogen atoms. This exercise reduces the number of basis functions per water molecule to 74.

It is clear from **Tables 1–4** that the decent basis set, viz. 6-31G(d,p) is good only for the initial structure optimization for larger clusters. Though the MUE for inter-action energies for various quantum chemical and DFT framework are large the overall trends and structures show qualitative trends similar to the other extended basis sets.

Taking a cue from the earlier studies [16, 54, 77] as well as the basic computational insights from the present investigation it may be concluded that the density functional theory in combination with appropriate basis sets can predict interaction energies at par or even with better accuracy when compared with MP2-level of theory. On the basis of review of earlier studies and present work, the density

Clusters	Str. Code	n_H	ΔE1	ΔE2	ΔE3	ΔE4	ΔE5	ΔE6	ΔE7	ΔE8	ΔE9	ΔE10	ΔE11
$(H_2O)_2$	—	1	−5.50	−7.50	−4.92	−5.37	−4.57	−4.95	−4.74	−5.17	−4.79	−4.98	−5.01
$(H_2O)_3$	—	3	−17.10	−25.00	−15.34	−16.49	−14.35	−15.45	−15.90	−17.03	−16.09	−15.8	−15.80
$(H_2O)_4$	—	4	−29.10	−41.70	−27.42	−28.85	−26.05	−27.76	−27.22	−28.76	−27.33	−27.6	−27.40
$(H_2O)_5$	—	5	−37.70	−53.30	−36.14	−37.86	−34.55	−36.76	−35.08	−37.32	−35.04	−36.3	−35.90
$(H_2O)_6$	Prism	9	−49.60	−72.00	−44.27	−48.59	−41.14	−44.33	−47.31	−50.04	−47.82	−45.9	−46.00
	Cage	8	−48.60	−70.70	−42.80	−48.34	−44.08	−44.60	−46.85	−49.43	−47.20	−45.8	−45.80
	Book	7	−47.75	−68.60	—	—	−44.84	−45.49	−44.94	−47.62	−45.09	−45.6	−45.30
	Ring	6	−46.58	−64.89	—	—	−44.63	−45.51	−43.08	−46.11	−43.36	−44.8	−44.30
$(H_2O)_8$	8A	12	−76.01	−110.64	−70.37		−68.28	−71.00	−73.63	−77.34	−74.54	−72.70	−72.60
	8B	12	−75.89	−106.96	−70.37		−66.24	−70.96	−73.62	−77.34	−74.52	−72.70	
$(H_2O)_{20}$	20A	36	−216.28				−184.10	−198.02	−211.80	−221.16	−212.56	−212.60	
	20B	34	−216.04				−188.85	−202.56	−206.03	−223.71	−209.16	−217.40	
	20C	35	−213.71				−185.75	−199.59	−207.72	−220.80	−210.96	−215.00	
	20D	33	−202.49				−185.75	−198.14	−192.76	−200.63	−187.60	−200.10	
	20E	30	−187.17										

ΔE1: ΔE at RHF/6-31G(d,p) level (Present work and Ref. [4]).
ΔE2: ΔE at B3LYP/6-31G(d,p) level (Present work and Ref. [4]).
ΔE3: ΔE at B3LYP/6-311++G(2d,2p) level (Present work and Ref. [4]).
ΔE4: ΔE at MP2/6-311++G(2d,2p) level (Present work and Ref. [4]).
ΔE5: ΔE at B3LYP/aug-cc-pVTZ level (Ref. [16]).
ΔE6: ΔE at X3LYP/aug-cc-pVTZ level (Ref. [16]).
ΔE7: ΔE at M06-L/aug-cc-pVTZ level (Ref. [16]).
ΔE8: ΔE at M06-2X/aug-cc-pVTZ level (Ref. [16]).
ΔE9: ΔE at M06/aug-cc-pVTZ level (Ref. [16]).
ΔE10: ΔE at MP2/CBS level (Ref. [16]).
ΔE11: ΔE at CCSD(T)/CBS level (Ref. [16]).
nH: Number of hydrogen bonds.

Table 1.
Comparison of interaction energies (in kcal.mol^{-1}) for $(H_2O)_n$, n = 2–6, with various model chemistries. (Refer text for details.)

	B3LYP	B3PW91	BHandHLYP	BLYP	HF	M06	M06-2X	M06-L	MP2	PBE0	τ-HCTHHYB	ωB97X	ωB97X-D
6-31G(d,p)	5.71	4.28	5.15	6.29	0.76	5.38	5.83	4.22	4.33	6.13	5.82	6.94	5.78
6-311++G(d,p)	1.00	0.14	1.61	0.30	1.32	2.27	2.67	1.54	1.36	1.93	1.37	3.27	2.07
6-311++G(2d,2p)	0.42	1.33	0.17	1.07	2.54	0.69	1.12	0.25	0.36	0.51	0.02	1.78	0.65
aug-cc-pVDZ	0.84	1.77	0.14	1.58	2.78	0.27	0.63	0.72	0.24	0.04	0.38	1.41	0.21
aug-cc-pVTZ	1.25	2.20	0.59	3.64	3.25	0.18	0.53	0.49	0.98	0.21	0.95	1.00	0.23
aug-cc-pVTZ-1	0.89	1.89	0.29	2.52	3.02	0.20	0.54	0.40	1.04	0.05	0.60	1.29	0.12
def2-TZVP	0.99	0.21	1.26	0.70	1.92	1.48	2.05	1.49	1.21	1.66	1.05	2.85	1.56

Table 2.

Mean unsigned errors (MUE) of interaction energies (in kcal/Mol), computed for $(H_2O)_2$ and $(H_2O)_3$ using various model chemistries. The reference energies were taken at CCSD(T)/aug-cc-pVQZ level (ref. [14, 26]).

	B3LYP	B3PW91	BHandHLYP	BLYP	HF	M06	M06-2X	M06-L
6-31G(d,p)	0.007	0.008	0.011	0.022	0.035	0.010	0.017	0.004
6-311++G(d,p)	0.005	0.003	0.013	0.017	0.042	0.009	0.010	0.006
6-311++G(2d,2p)	0.008	0.006	0.006	0.025	0.054	0.002	0.003	0.003
aug-cc-pVDZ	0.008	0.006	0.007	0.025	0.051	0.003	0.003	0.007
aug-cc-pVTZ	0.009	0.008	0.006	0.023	0.055	0.007	0.002	0.003
aug-cc-pVTZ-1	0.009	0.008	0.007	0.023	0.056	0.003	0.001	0.002
def2-TZVP	0.006	0.006	0.008	0.023	0.048	0.004	0.002	0.005
	MP2	**PBE0**	**τ-HCTHHYB**		**ωB97X**	**ωB97X-D**		
6-31G(d,p)	0.126	0.014	0.014		0.012	0.006		
6-311++G(d,p)	0.004	0.012	0.012		0.014	0.010		
6-311++G(2d,2p)	0.005	0.005	0.006		0.007	0.003		
aug-cc-pVDZ	0.011	0.009	0.011		0.010	0.006		
aug-cc-pVTZ	0.005	0.007	0.008		0.008	0.003		
aug-cc-pVTZ-1	0.006	0.005	0.005		0.007	0.002		
def2-TZVP	0.005	0.008	0.007		0.003	0.007		

Table 3.
Mean unsigned errors (MUE) for bond lengths (in) computed for $(H_2O)_2$ and $(H_2O)_3$ using various model chemistries. The reference structural parameters were taken from the experimental data (ref. [76]).

	B3LYP	B3PW91	BHandHLYP	BLYP	HF	M06	M06-2X	M06-L
6-31G(d,p)	3.31	2.35	2.06	5.07	1.30	3.74	2.84	3.45
6-311++G(d,p)	1.64	1.48	2.36	1.04	3.71	1.72	1.58	1.25
6-311++G(2d,2p)	0.71	0.70	1.27	0.36	2.06	0.73	1.27	0.49
aug-cc-pVDZ	0.41	0.38	1.11	0.35	2.22	1.01	0.73	0.69
aug-cc-pVTZ	0.67	0.57	0.98	0.55	2.06	0.97	0.68	0.43
aug-cc-pVTZ-1	0.79	0.60	1.48	0.40	2.67	0.65	0.44	0.66
def2-TZVP	1.20	1.17	2.00	0.38	3.24	1.55	0.49	0.24
	MP2	**PBE0**	**τ-HCTHHYB**		**ωB97X**	**ωB97X-D**		
6-31G(d,p)	2.66	3.01	2.94		3.30	2.79		
6-311++G(d,p)	2.49	1.41	1.43		1.48	1.61		
6-311++G(2d,2p)	1.21	0.32	0.32		0.72	0.50		
aug-cc-pVDZ	0.37	0.14	0.22		0.36	0.43		
aug-cc-pVTZ	0.46	0.31	0.38		0.42	0.35		
aug-cc-pVTZ-1	0.35	0.47	0.54		0.48	0.42		
def2-TZVP	0.81	0.95	1.04		1.19	1.21		

Table 4.
Mean unsigned errors (MUE) for bond angles (in degrees) computed for $(H_2O)_2$ and $(H_2O)_3$ using various model chemistries. The reference structural parameters were taken from the experimental data (ref. [76]).

functionals recommended to study water clusters are: MN15 [16, 54, 77], ωB97X-D, M06, M06-L, M06-2X and the broad applicability density functional, viz. PBE0. The recommended basis set should be triple zeta-quality viz. aug-cc-pVTZ,

aug1-ccp-VTZ and def2-TZVP. A comparison of the interaction energy of $(H_2O)_2$ computed with various model chemistries is given in **Table 5**.

It is clear from the **Table 5** that the truncated basis set, viz. aug1-cc-pVTZ yield interaction energies that are at par with its parent basis set viz. aug-cc-pVTZ. However, the reduction in number of basis functions results in boosting the speed of computation by a factor of ~2.0 or more for the geometry optimization as well as vibrational frequency computations of water trimer $(H_2O)_3$. This is expected to boost-up further for larger clusters. Thus, aug1-cc-pVTZ basis set is recommended for DFT-study on water clusters.

The vibrational frequency analysis of smaller clusters viz. $(H_2O)_n$, where n = 1–4 show shift as well as splitting of vibrational infra-red)IR) frequencies with successive addition of water molecules. The H-O-H bending frequency shows blue-shifts whereas stretching frequencies (symmetric and asymmetric stretching) show red-shift with successive addition of water molecules. This feature is akin to the earlier studies [4, 51, 78]. The vibrational frequency analysis for smaller clusters upto tetramer performed with PBE0/aug1-cc-pVTZ model chemistry is given in **Table 6**. Also, the successive addition is associated with increase in the spectral intensity. The increase in spectral intensity is an indication of charge separation which may be seen in terms of increase in number of hydrogen (denoted by nH in **Table 1**) with addition of water molecule to the given cluster.

The review of the present literature also reveals that the energetic stability of smaller clusters $(H_2O)_n$ with $n \leq 10$ are predominantly dependent on the total number of hydrogen bonds (HBs) in the given cluster. These hydrogen bonds are the manifestation of donor-acceptor (da) arrangement of water molecules. In case of two dimensional structures the $(H_2O)_n$ clusters with maximum number of donor-acceptor type of hydrogen bonds are energetically more favorable. Hence,

Method	Basis set	ΔE (kcal/mol)	Absolute Error (kcal/mol)
Expt.		−5.000[a]	0.000
CCSD(T)	aug-cc-pVTZ	−5.217[a]	0.217
	aug-cc-pVQZ	−5.101[a]	0.101
	aug-cc-pV5Z	−5.034[a]	0.034
M06-2X	aug-cc-pVTZ	−5.172	0.172
	aug-cc-pVTZ-1	−5.172	0.172
	def2-TZVP	−5.932	0.932
MP2	aug-cc-pVTZ	−5.181	0.181
	aug-cc-pVTZ-1	−5.037	0.037
	def2-TZVP	−5.664	0.664
PBE0	aug-cc-pVTZ	−5.219	0.219
	aug-cc-pVTZ-1	−5.007	0.007
	def2-TZVP	−5.920	0.920
wB97X-D	aug-cc-pVTZ	−5.014	0.014
	aug-cc-pVTZ-1	−5.022	0.022
	def2-TZVP	−5.854	0.854

[a]*Energy values adapted from Ref. [16].*

Table 5.
Interaction energy (in kcal.Mol^{-1}) of water dimer, $(H_2O)_2$ computed with various model chemistries.

Vibration modes assigned	H_2O	$(H_2O)_2$	$(H_2O)_3$	$(H_2O)_4$
H-O-H bending	1634.2 (78.3)	1634.6 (95.7)	1645.1 (64.8)	1648.7 (93.9)
		1655.1 (95.8)	1648.1 (98.8)	1663.0 (51.1)[D]
			1670.1 (18.6)	
O-H symmetric stretch	3864.1 (6.8)	3720.9 (357.8)	3547.5 (16.5)	3435.6 (1634.9)[D]
		3853.7 (13.6)	3617.8 (644.7)	3479.1(21.1)
			3630.5 (597.0)	
O-H asymmetric stretch	3969.7 (66.9)	3935.6 (84.7)	3925.6 (95.9)	3924.2 (98.9)
		3955.5 (96.0)	3929.6 (96.2)	3924.9 (90.9)[D]
			3931.1 (48.3)	

[D]*Degenerate (Doublet).*

Table 6.
Vibrational frequencies (in cm^{-1}) computed at PBE0/aug1-cc-pVTZ optimized geometries for $(H_2O)n$, n = 2, 3, and 4: Results for water monomer included for comparison. Values in the parentheses indicate intensities.

the cyclic oligomers up to pentameric water clusters are energetically more favorable than their acyclic or linear chain counterparts. Also, these cyclic structures of tetramer, pentamer and hexamer form the basic building blocks for the energetically favorable larger clusters viz. $(H_2O)_n$, for n = 12, 15, 16, 20, 24, 25, 30 and so on. The hexameric ring even though energetically unfavorable as compared to prism and cage hexamers also forms the basic building blocks of higher clusters viz. $(H_2O)_n$, n = 12, 18, 20, 24, 30 and so on.

As concluded by the earlier studies [4], that one can anticipate several structures for a given water cluster $(H_2O)_n$, by changing the hydrogen bonding sequence. Hence, the number of possible energetically favorable isomers increase very fast with increase in the value of n. Considering all such isomers in a single study is beyond the scope of a single study.

4. Conclusions

The present short review on investigation of water clusters employing DFT-framework delineates the strength of DFT to study water clusters accurately and efficiently. The salient features of the present work are summarized as follows.

DFT in conjugation with appropriate triple zeta basis set can yield very accurate estimation of interaction energies and structures of water clusters. The results are at par with MP2/CBS or even CCSD(T)/CBS level of theory. The recommended density functionals for studying water clusters are MN15 [16, 54, 77], ωB97X-D, M06, M06-L, M06-2X and PBE0 where the recommended basis sets is aug-cc-pVTZ. The truncated basis set aug1-cc-pVTZ can also yield better agreement of interaction energies when compared with MP2/CBS and CCSD(T)/ CBS levels of theory. Hence, it is recommended for studying the larger clusters as well as lowering the computational exhaustiveness of the calculations. The cyclic structures of tetramer, pentamer and hexamer are the basic building blocks of larger clusters.

The performance of DFT in studying water clusters is indeed encouraging. It is expected that the initial guidelines from the present short-review can be gainfully employed to investigate larger water clusters and assessment of additional density functionals.

The investigations combined with the novel approaches like molecular tailoring approach will enable in obtaining the better understanding and accurate prediction of interaction energies within DFT-framework. Such studies are underway and will be undertaken in an independent venture.

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