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Hydrogen Bonding Patterns in Water Clusters: Trimer, Tetramer and Pentamer

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Hydrogen Bonding Patterns in Water Clusters: Trimer, Tetramer and Pentamer[#]

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Abstract

In elucidating the thermodynamic properties, it is important to know all the possible structures in an aggregated system. Water molecules are assembled in a water cluster and form a hydrogen bond network. The most important feature of the hydrogen bond is that it possesses the direction. To represent the feature of the hydrogen bond, we use digraphs. All the possible topology–distinct hydrogen bonded structures for water trimer, tetramer and pentamer, $(H_2O)_n$ (n = 3–5), are enumerated by means of digraphs and all the corresponding digraphs are shown. Using those structures as the theoretical framework, the local minima on the potential energy surfaces of those water clusters are obtained using the *ab initio* MO method at the HF/6–31G* level of theory. The electron density maps are also calculated. It is shown that the hydrogen bonding pattern as well as the number of the hydrogen bonds influences the stability of a water cluster.

Keywords. Water cluster; hydrogen bond; *ab initio* MO; graph theory; digraph; electron density map.

Abbreviations and notations	
au, atomic unit	HF, Hartree–Fock
H–bond, hydrogen bond	MO, molecular orbital
H–B matrix, hydrogen bond matrix	MP2, second order Møller–Plesset perturbation theory

1 INTRODUCTION

Although hydrogen bonds are weaker than covalent bonds, they can form long–lived structures of water clusters. There are a lot of locally stable structures in water clusters with various arrangements of the constituent water molecules. The number of the available structures (the H–bond patterns) plays an important role in thermodynamic properties of water clusters.

In elucidating the thermodynamic properties, it is important to know all the possible structures and their relative energies in an aggregated system. Water molecules are assembled in a water cluster and form an H–bond network. There have been many studies to search global minima of water clusters by means of the shift method [1], the genetic algorithm method [2], Monte Carlo–

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based methods [3–6] and other methods [7,8], using the empirical potential functions or using MO methods. Many recent studies have used Monte Carlo sampling or Monte Carlo–based simulated annealing procedures, though it is not guaranteed that all possible configurations are indeed sampled in those simulations. The eigenmode method has been used for locating stationary structures of water clusters, and a large number of local minima have been located for water clusters $(H_2O)_n$ ($n \leq 6$) [9,10]. The number of local minima increases rapidly with the cluster size. A graph theoretical technique has been introduced to generate water cube and dodecahedral clusters for $(H_2O)_8$ and $(H_2O)_{20}$ [11,12], and water cage clusters for $(H_2O)_6$ [12,13]. It is not trivial to present all the possible structures or to claim that a structure is indeed the global minimum.

The characteristic feature of the H–bond is that it possesses the direction; in an H–bond, a hydrogen atom is "donated" to an acceptor (oxygen atom). The direction can be indicated by an arrow. In our previous study [14], we have presented a graph theoretical procedure to generate all the topology–distinct structures of water clusters by means of the digraph representation. A digraph corresponds to an H–bonded structure; the pattern of H–bond connections corresponds to the set of arrows (Figure 1).
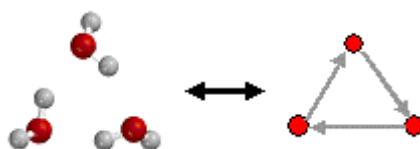

Figure 1. Structure of water cluster and the corresponding digraph.

In this paper we give all possible topology–distinct patterns of the H–bond connections and the local minima on the potential surfaces of $(H_2O)_n$ ($n = 3–5$). The number of the local minima might vary when a different level of MO theory or any potential function is used for the calculation of the potential surface. The important point is that we know all the possible topology–distinct H–bond patterns of water clusters after the enumeration; *i.e.*, we know that there cannot be other patterns.

2 MATERIALS AND METHODS

A graph is a mathematical structure and represents the topology of a molecule. A graph is a set of vertices and edges. A graph has the corresponding matrix representation. Molecular structures can be represented with graphs, where vertices correspond to atoms, and edges correspond to bonds. For a graph with *n* vertices, the adjacency matrix **A** is the *n*–th order square matrix, whose element a_{ij} is equal to 1 for a pair of vertices *i* and *j* which are connected by an edge, and 0 otherwise. The most important feature of the H–bond is that it possesses the direction. To represent the feature of the H–bond, we use a digraph. A digraph (directed graph) is a set of vertices and arcs. A digraph has the corresponding matrix representation. For a digraph with *n* vertices, the directed adjacency matrix H is the *n*–th order square matrix, whose element h_{ij} is equal to 1 for an arc directed from

vertex *i* to vertex *j*, and 0 otherwise. Water clusters can be represented by digraphs, where vertices correspond to water molecules, and arcs correspond to hydrogen bonds from proton–donor to proton–acceptor (see Figure 1). We call the representative directed adjacency matrix 'H–B matrix'. All the possible structures which are topology–distinct can be obtained by means of the H–B matrix, *i.e.*, by counting up all the possible digraphs with the conditions of forming water clusters. The procedure to enumerate all possible topology–distinct structures of water molecules is described in detail elsewhere [14].

Any local minimum on the potential surface of a water cluster must belong to one of all the topology–distinct H–bond patterns. For each of the H–bond patterns up to water pentamer, we constructed various trial initial geometries by use of a graphical tool of Mac Spartan Pro [15]. For each of the trial geometries, we performed the geometry optimization by means of the *ab initio* MO method at the HF/6–31G* level of theory. We obtained all the optimized structures which are topologically distinguishable for each of $(H_2O)_n$ (n = 3–5). The program packages of HONDO [16] and Spartan [15] were used for the *ab initio* MO calculations.

3 RESULTS AND DISCUSSION

We have enumerated the digraphs containing 3, 4 and 5 vertices, which correspond to water trimer, tetramer and pentamer, $(H_2O)_n$ (n = 3–5). It should be noted here that we deal with only topology–distinct geometries in the current work. We do not take account of any fine structures of water clusters, such as the direction of a free O–H bond [17].

3.1 Water Trimer

The number of the topology–distinct hydrogen bonding patterns of the water trimer is 5. The corresponding digraphs are shown in Figure 2.
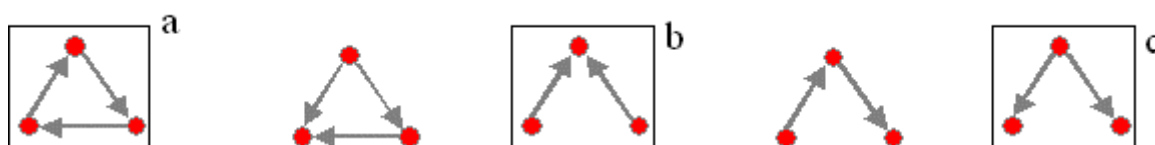

Figure 2. Digraphs with 3 vertices.

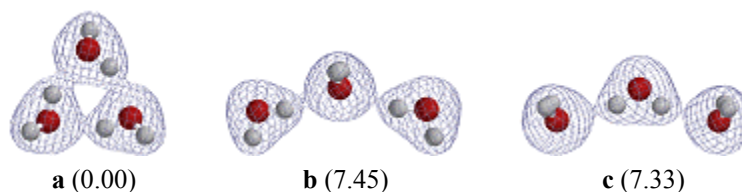**a** (0.00)   **b** (7.45)   **c** (7.33)

Figure 3. Geometries and electron density surfaces of water trimers. Numbers in parentheses indicate the total energies relative to the most stable isomer **a** in kcal mol^{-1}. Electron density contour shown is the surface of 0.02 electrons au^{-3}.

The set of the digraphs in Figure 2 includes all the possible hydrogen bonding patterns of the water trimer, which are topology–distinct. We constructed various trial initial geometries for a water trimer with a hydrogen bonding topology corresponding to each of the above digraphs, and we performed the geometry optimization by means of the *ab initio* MO method at the HF/6–31G* level of theory. Local minima on the potential surface were found for three of the five patterns, which are denoted as **a** – **c** in Figure 2, and the geometries are shown in Figure 3 with each electron density map. Electron density contour shown is the surface of 0.02 electrons/au^3.

The most stable isomer of the water trimer is the cyclic one, **a**; **c** is less stable than **a** by about 7.3 kcal/mol. The stability of **b** is very similar to that of **c**. Since the number of the hydrogen bonds in a cyclic isomer is larger than that of a linear isomer, it may be no surprise that a cyclic isomer is more stable than a linear isomer in the water trimer. It is interesting, however, to see that the electron density between a proton donor and a proton acceptor in the cyclic isomer **a** is higher than that in either of the linear isomers **b** and **c**. This suggests that the hydrogen bonds in the cyclic isomer **a** are stronger than those in **b** and **c**.

Tsai and Jordan [9] showed that the number of the local minima for water trimers is 3 (Figure 20 of [9]) by means of the eigenmode method using the TIP3P potential [18], while the number of the topology–distinct local minima which we have found in the current work is larger than that found in [9]. The number of the local minima on the potential surface should vary with the potential function or the level of the MO theory used. The important point in our work is that we know all the possible topology–distinct hydrogen–bonding patterns. We know that there are no patterns for the water trimer other than those in Figure 2.

The level of the *ab initio* MO theory which we used for the potential energy calculation in the current work is not high enough to deal with the hydrogen bonding interaction quantitatively. It is worthy of note, however, that the local minima and the order of their relative stabilities (Figure 3) are the same as those presented by Xantheas [19] at the MP2/aug–cc–pVDZ level of theory with taking account of the basis set superposition error.

3.2 Water Tetramer

The number of the topology–distinct hydrogen bonding patterns of the water tetramer is 22. The corresponding digraphs are shown in Figure 4. We have found that 5 out of 22 correspond to the stable structures of water tetramers. The optimized structures of water tetramers are shown in Figure 5. The obtained structures are topologically the same as those found by a Monte Carlo procedure [6] using the MCY [20] and CCD [21] potentials. The 4–membered cyclic cluster **d** is the most stable tetramer, and cluster **e** is less stable by 12.4 kcal/mol. The 4–membered cyclic structures (**d** and **e**) are generated from the identical non–directed graph and both have 4 hydrogen bonds, though the combination in the directions of the hydrogen bonds is different.
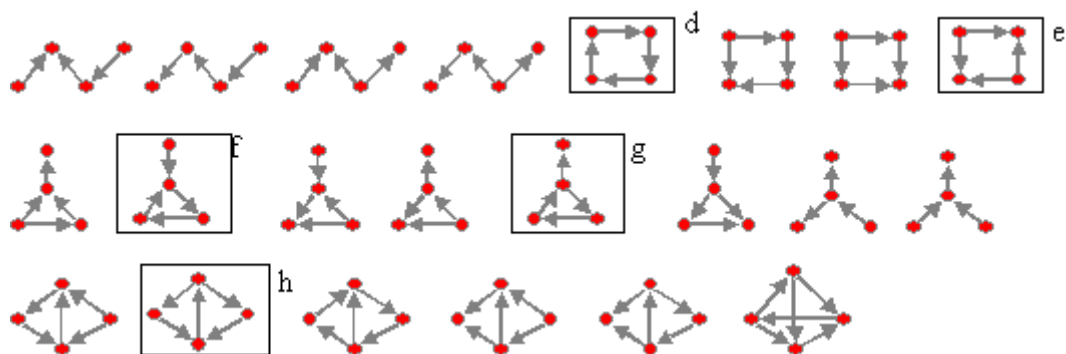
Figure 4. Digraphs with 4 vertices.

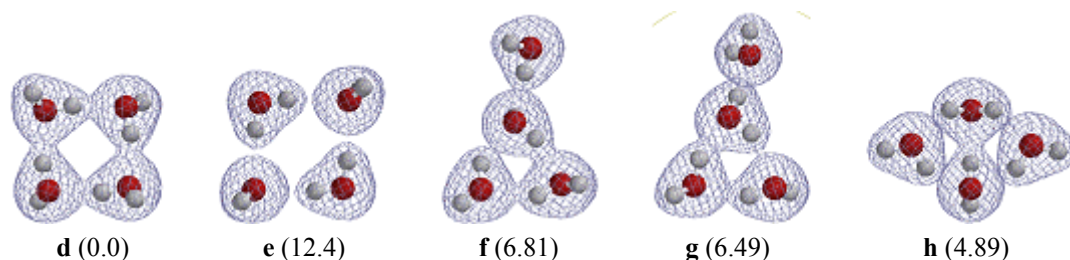| **d** (0.0) | **e** (12.4) | **f** (6.81) | **g** (6.49) | **h** (4.89) |

Figure 5. Geometries and electron density surfaces of water tetramers. Numbers in parentheses indicate the total energies relative to the most stable isomer **d** in kcal mol^{-1}. Electron density contour shown is the surface of 0.02 electrons au^{-3}.

We note that the electron density in the H–bond region in the more stable cyclic tetramer **d** is quite high, in contrast to that in the less stable cyclic tetramer **e**. It looks that an H–bond pattern in which a larger number of the arrows (the directions of the H–bonds) are in the same direction is stable. At the MP2/aug–cc–pVDZ level of theory, Xantheas [19] showed that the energy of the ring minimum of D_{2h} symmetry (the structure **e** in the current work) was higher than the cyclic structure of S_4 symmetry (the structure **d** in the current work) by 10.5 kcal/mol, where almost 2/3 came from the three–body terms with the remaining 1/3 due to the two–body terms. It should be noted that a digraph (which is equivalent to an H–bond pattern) contains the information concerning not only the two–body but also the three–body and higher terms of the hydrogen bonding energy in a water cluster. It is probable that the H–bond pattern influences the relative stability of a water cluster.

3.3 Water Pentamer

The number of the topology–distinct hydrogen bonding patterns of the water pentamer is 161. The corresponding digraphs are shown in Figure 6.

We have found that 21 out of 161 correspond to the stable structures of water pentamers. The optimized structures of water pentamers and their relative energies are shown in Figure 7. Eleven out of these 21 structures have already appeared in literatures [6–9], which are indicated by dotted squares in Figure 7. We have found many new structures for the water pentamer. Electron density contour maps are shown for the 21 structures in Figure 8.
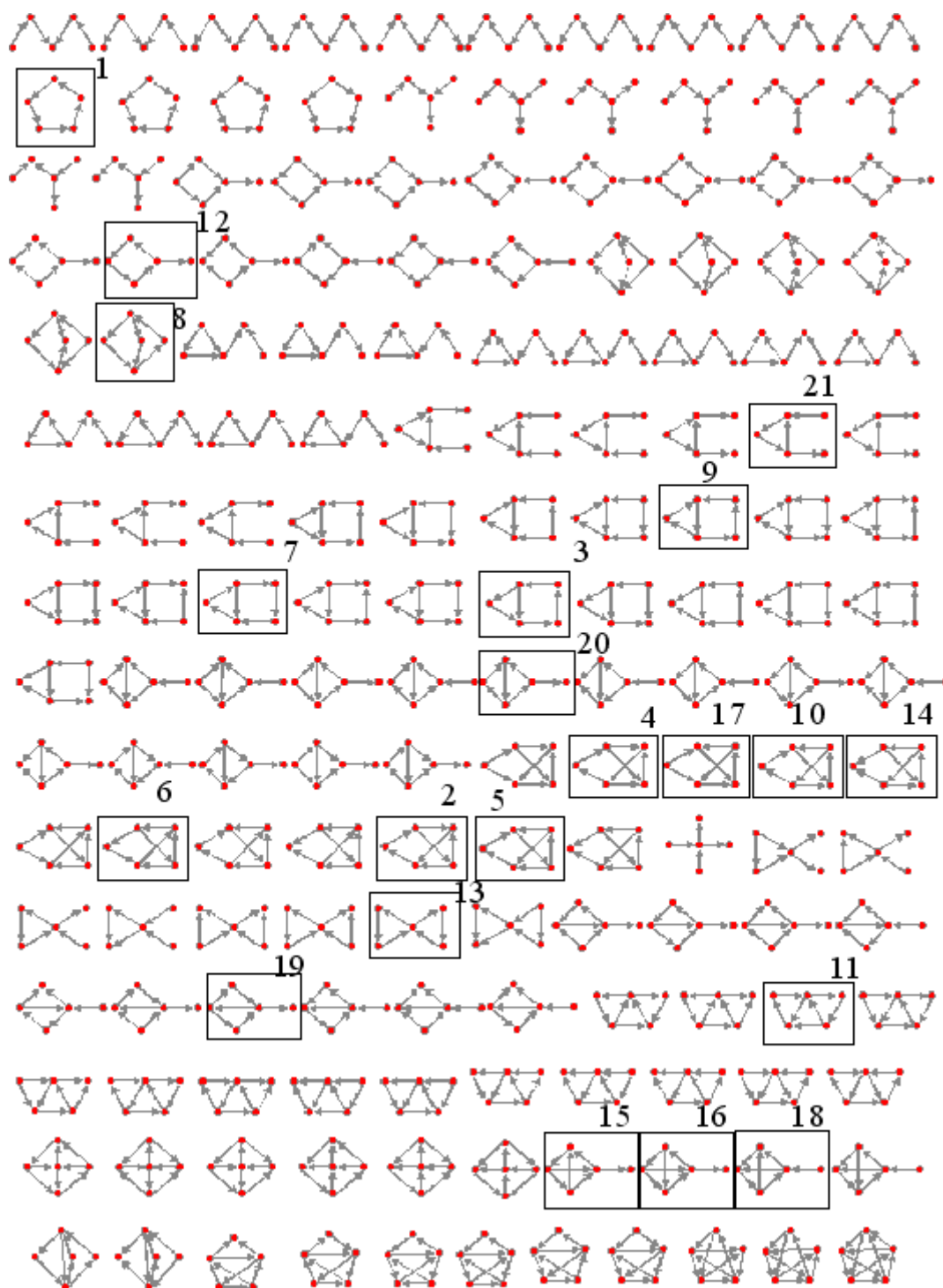
Figure 6. Digraphs with 5 vertices. The digraphs with numbering correspond to the structures shown in Figures 7 and 8.

The 5–membered cyclic cluster is the most stable pentamer. The H–bond network in the most stable cyclic isomer is comprised of the high electron density H–bond regions; in contrast, there are some 'nodes' in less stable isomers. It looks as if some of the water molecules are independent in less stable isomers. Since there are many structures for water pentamers that are very close in energy, the order of the relative energies may change when a higher level *ab initio* method is

applied. The results presented here should be viewed as illustrating the utility of the enumeration of the H–bond patterns rather than providing a detailed quantitative characterization of the stationary points of water clusters.
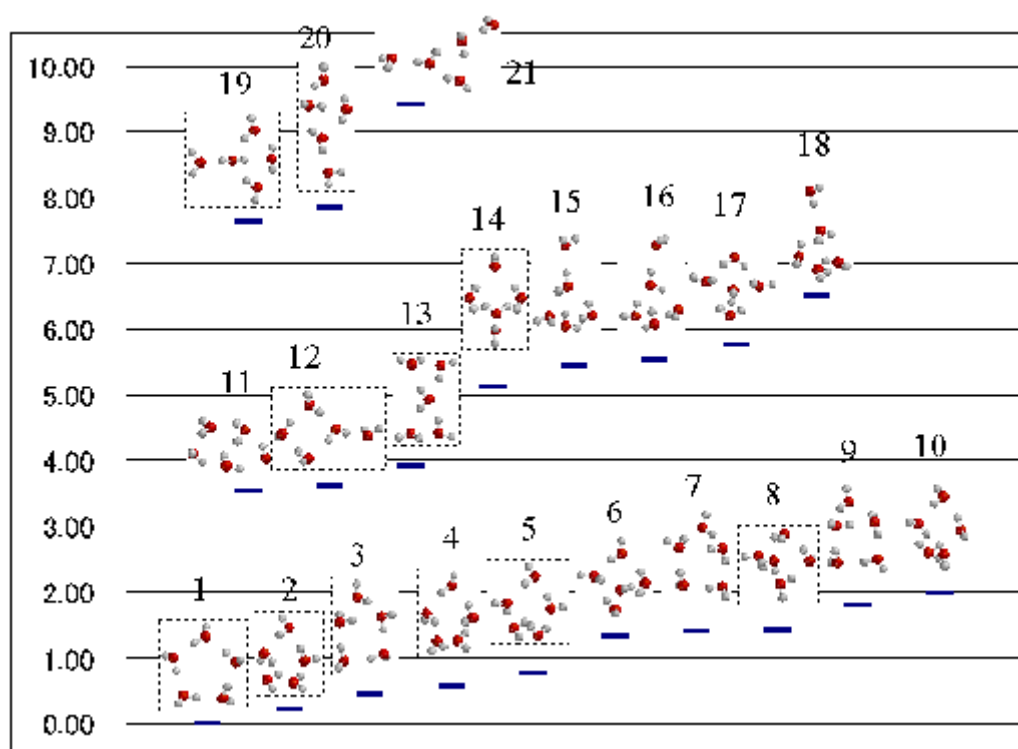

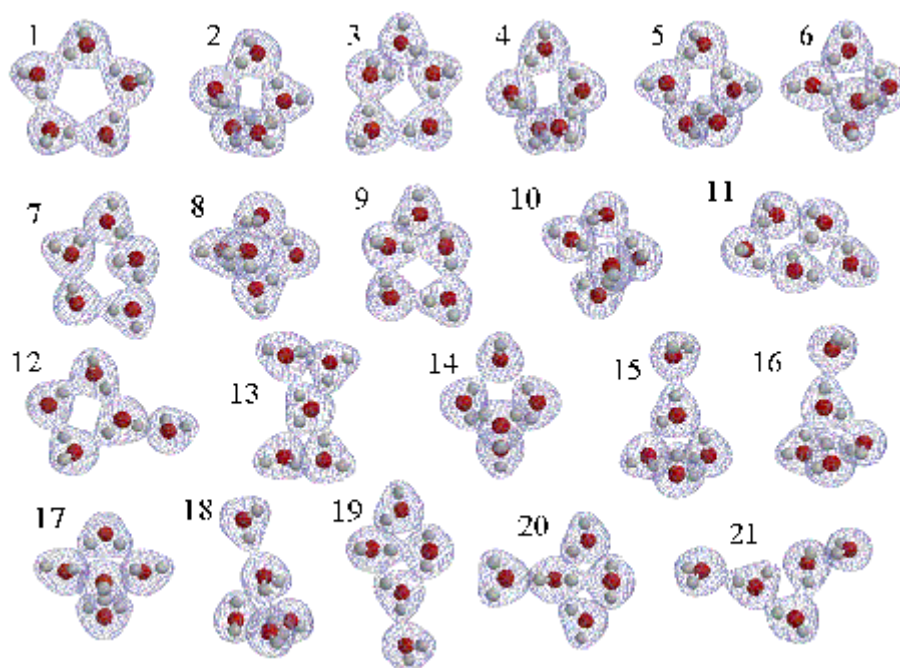**Figure 7.** Relative energies (in kcal/mol) of the stable structures of water pentamers.

Figure 8. Electron density maps of stable structures of water pentamers. Electron density contour shown is the surface of 0.02 electrons/au^3.

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4 CONCLUSIONS

The enumeration of digraphs is a useful method to present all the possible topology–distinct hydrogen bond patterns of water clusters. The local minima on the potential energy surfaces of those water clusters can be obtained using those patterns as the theoretical framework. We have found many stable structures which were not known in literatures. The number of the local minima might vary when a different level of theory is used for the geometry optimization. The important point in the current work is that we know *all* the possible topology–distinct H–bond patterns of water clusters after the enumeration; *i.e.*, we know that there cannot be other patterns. A digraph corresponding to a water cluster contains the H–bond information that includes not only the two–body pair wise terms but also the three–body and higher terms. The H–bond pattern, as well as the number of the H–bonds, influences the stability of a water cluster.

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Biographies

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