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Bonding Analysis of Water Clusters Using Quasi-Atomic Orbitals

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Abstract: The quasi-atomic orbital (QUAO) bonding analysis introduced by Ruedenberg and co-workers is used to develop an understanding of the hydrogen bonds in small water clusters, from the dimer through the hexamer (bag, boat, book, cyclic, prism and cage conformers). Using kinetic bond orders as a metric, it is demonstrated that as the number of waters in simple cyclic clusters increases, the hydrogen bonds strengthen, from the dimer through the cyclic hexamer. However, for the more complex hexamer isomers, the strength of the hydrogen bonds varies, depending on whether the cluster contains double acceptors and/or double donors. The QUAO analysis also reveals the three-center bonding nature of hydrogen bonds in water clusters.

1. Introduction:

Water has been the subject of many scientific studies, in large part because it is naturally occurring, it plays a key role in the life sciences, it is fundamental in a wide range of industrial processes, and it has had a large influence in the development of life itself(1). Understanding water is central to unraveling many aspects of solution chemistry. Nonetheless, this seemingly simple molecule is not yet fully understood.(2) Water possesses strong polar hydrogen bonds that are responsible for many of its chemical and physical properties; it has been studied extensively in the gas and condensed phases using both theory(3–16) and experiments(3,17–22). Further information on the unusual properties of water and other experimental results can be found in references (8,23–25).

Water clusters have been shown to play a role in the formation of acid rain and in anomalous absorption of sunlight by clouds and the nucleation of water droplets. Indeed, it has recently been reported that individual water molecules (possibly clusters) have been detected on the lunar surface(26). In addition, water clusters are simple systems for analyzing cooperativity and anti-cooperativity effects(27–29) and hydrogen bonding rearrangement dynamics.(2,9)

Hydrogen bonds have variously been interpreted as 90% electrostatic and 10% covalent interactions(30), and alternatively as a mixture of electrostatic, charge transfer, and dispersion interactions(23). The energy of a hydrogen bond varies as a function of the system(31). For example, the hydrogen bond energy in hydrogen halides (Cl, Br) ranges from ~8 to 22.0 kcal/mol, while the difluoride (FHF^-) binding energy is ~44.4 kcal/mol.(32,33)

Bonding analyses have been performed on hydrogen bonded systems, both with the quantum theory of atoms in molecules (QTAIM)(34–40), and with the natural bond orbital (NBO) method(41,**42**). QTAIM provides two dimensional images, topological maps of the bonding structure, and an interpretation of the bonding in the molecules. The NBO analysis of intermolecular interactions has recently been questioned by Stone(41,43,44), specifically regarding the charge transfer contribution to the hydrogen bond energy.

Recently, a quasi-atomic bonding analysis was developed(45–48) in terms of intrinsic atomic orbitals (AOs). The intrinsic AOs are obtained by projections of the molecular wave function onto highly accurate atomic orbitals. The resulting orbitals, called quasi-atomic orbitals (QUAOs) are AOs that are deformed by the chemical environment of the molecule (relative to orbitals in the free atom) and have maximal overlap with the original AOs. The QUAO method provides quantitative information about the broad array of bond types in terms of orbital occupations, bond orders, and the kinetic bond orders which reflect the fundamental origins of chemical bonds. The method has been used to understand the bonding motifs of several molecules, including a suite of organic molecules,(47) rare gas-containing molecules,(49) organozirconium complexes(50), cerium oxides,(51,52) and to explore the decomposition pathway of dioxetane.(48)

The present study provides insight into the nature of hydrogen bonding in water clusters $(H_2O)_n$ (n=2-6) using the QUAO bonding analysis. The relevant aspects of the methods are summarized in Section 2. The results of the analysis of hydrogen bonding in water clusters are discussed in Section 3. Conclusions are drawn in Section 4.

2. Methods:

2.1 Quasi-atomic orbital localization

The quasi-atomic orbital analysis is implemented in the GAMESS suite of electronic structure programs.(53,54) Only the most relevant details are summarized here.

A set of orbitals that are quasi-atomic in character is obtained by maximizing the projection of molecular orbitals from, e.g., a Hartree-Fock (HF) wave function, onto an accurate atomic minimal basis set (AAMBS) of orbitals.(45) The expression of the first order density matrix in terms of the quasi-atomic orbitals is:

$$\rho(1,2) = \sum_{Aa}\sum_{Bb} |Aa(1)\rangle p_{Aa,Bb} \langle Bb(2)| \ \#(1)$$

In Eq. (1) $|\mathrm{Aa}\rangle$ is the a^{th} quasi-atomic orbital on atom A and p_{AaBb} is an element of the density matrix **p** that corresponds to the occupation of $|\mathrm{Aa}\rangle$ when Bb = Aa or to the bond order between $|\mathrm{Aa}\rangle$ and $|\mathrm{Bb}\rangle$ otherwise. The matrix **p** is called the population/bond order-matrix.(46) The maximum possible value of an occupation is 2, and the maximum possible absolute value of a bond order is 1.(55)

Linear combinations of the QUAOs are formed in a manner that minimizes the number of large bond orders. These "chemically adapted" QUAOs are called *oriented* quasi-atomic orbitals, or simply QUAOs from this point onward.

For diatomic molecules, the positive off-diagonal elements of the **p** matrix represent covalent bonding interactions, whereas negative ones represent antibonding interactions between the oriented QUAOs. However, for polyatomic systems this is not necessarily the case. It is difficult to control the phases of orbitals, so bonding interactions may be associated with a negative bond order. Additionally, bond orders do not directly provide any energetic information. West et al introduced kinetic bond orders (KBOs)(46), which are obtained by taking the product of the bond orders and the interference kinetic energy integrals between the corresponding interacting QUAOs., multiplied by a scaling factor of 0.1:

$$KBO_{Aa,Bb} = 0.1 p_{Aa,Bb} \left\langle Aa \right| -\tfrac{1}{2}\nabla^2 \left| Bb \right\rangle \qquad (2)$$

Since the interference kinetic energy drives the formation of covalent bonds(56), the KBOs provide a measure of the relative strengths of bonds. The KBOs are always negative for bonding interactions(57), regardless of the phases of the respective QUAOs. Bond orders and (especially) kinetic bond orders are the most representative quantities produced by the QUAO scheme and are used in the following to analyze the bonding interactions in the water clusters.

2.2 Computational details

The structures for the tetramer, pentamer, and hexamer isomers were obtained from a previous study based on MP2/aug-cc-pVTZ geometry optimizations.(7) The structures for the water dimer and trimer were optimized at the MP2/aug-cc-pVTZ level of theory to be consistent with the rest of the water clusters. Nuclear Hessian calculations verified that the structures obtained are local minima on the respective potential energy surfaces. All calculations were done using the GAMESS quantum chemistry program.(53) The QUAO analysis is based on the Hartree-Fock orbitals. All of the QUAO figures were obtained with the visualization program MacMolPlt(58). The contour values correspond to 0.1 (electron/bohr^3)$^{1/2}$. No symmetry was imposed for the geometry optimizations.

3. Results and Discussion:

The convention for QUAO notation is as follows: The first component is the (upper case) atomic symbol on which the QUAO is centered. If this QUAO participates in a bond the next symbol, in lower case, is the atomic symbol of the atom with which the first QUAO forms a bond. The Greek letter σ is used to represent a σ type orbital, and a lower-case h is used to indicate a hydrogen bond. Each atom carries the appropriate numerical subscript as well. Examples are:

- $O_xh_y\sigma$ represents a QUAO on oxygen atom x that forms a σ bond between oxygen atom x and hydrogen atom y
- H_xo_yh represents a QUAO on hydrogen atom x that forms a hydrogen bond between hydrogen atom x and oxygen atom y (this notation does not necessarily imply a two-center interaction)
    - O_x*lp* represents a QUAO for a lone pair on oxygen atom x
- H_x—o_yh_z will be used to represent networks. For example,
    - H_x—o_yh_z--o_ih_j represents a hydrogen bond between hydrogen x and oxygen y, linked with hydrogen z bonded to oxygen i through hydrogen bonding. (see Figure 1c caption)

Some useful definitions:

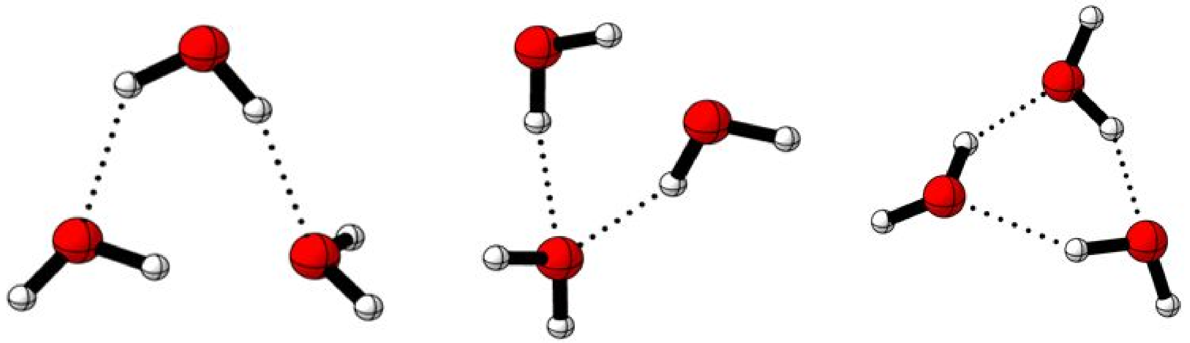
- Double acceptor: A water molecule whose oxygen atom receives two hydrogen bonds
    - For simplicity a double acceptor bond can be labelled as: $H_{x(y)}o_zh$ which means that oxygen atom z is accepting hydrogen bonds from hydrogen atoms x and y
- Double donor: A water molecule whose two hydrogen atoms are involved in hydrogen bonding

  - $O_xh_{y(z)}h$ means oxygen atom x is bonded to hydrogen atoms y and z, which are involved in hydrogen bonding (see Figure 1a)

- Homodromic network: hydrogen bonding networks with double donors and double acceptors present(5)

Figure 1 shows examples of a double donor and a double acceptor. A water molecule producing two hydrogen bonds (Figure 1a) is a double donor, and a water molecule accepting two hydrogen bonds (Figure 1b) is a double acceptor. To distinguish between the two types of σ bonds in water clusters, the following notation is used:

- (o) represents a bond not participating in a hydrogen bond. For example, OHσ(o) represents a sigma bond in which the H does not form a hydrogen bond.
- (i) represents a bond participating in a hydrogen bond. For example, OHσ(i) represents a sigma bond in which the H forms a hydrogen bond to another O.
- *H* represents a hydrogen bond.
- *lp* represents a lone pair QUAO



a) Double donor b) Double acceptor c) Sample network

Figure 1. Examples of a water molecule acting as double donor (a) and a double acceptor (b), and a hydrogen bonding network (H_x-o_yh_z-o_ih_j) (c)

3.1 Dimer – Pentamer Clusters

The optimized geometries of the dimer, trimer, tetramer, and pentamer are shown in Figure 2. In all systems, each water molecule donates or accepts one H to form a hydrogen bond. The oxygen atoms in the trimer, tetramer and pentamer are coplanar.

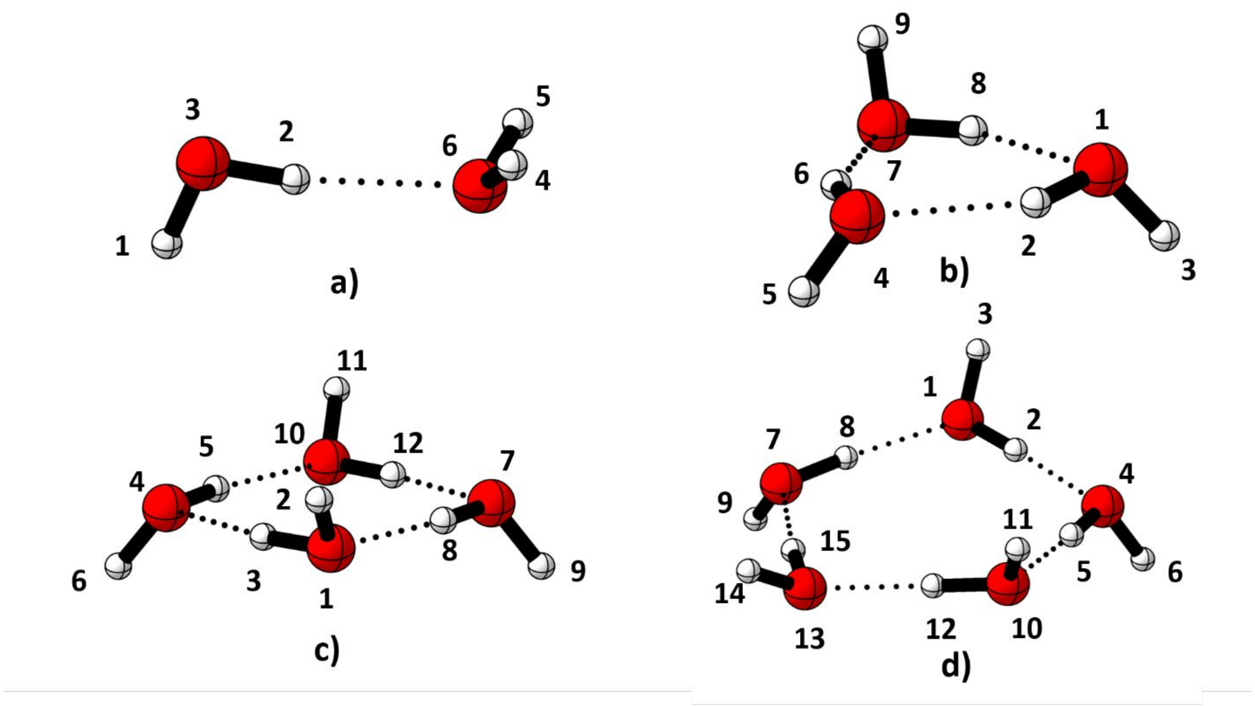
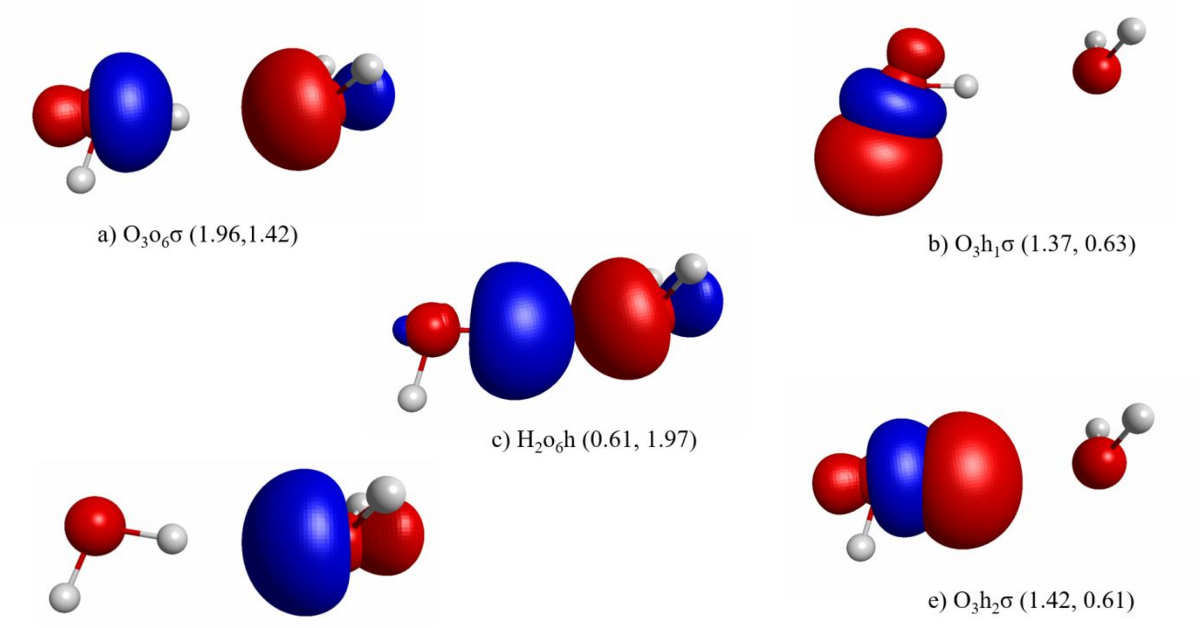


Figure 2. MP2/aug-cc-pVTZ optimized geometries of the water a) dimer, b) trimer, c) tetramer, and d) pentamer.

Localized Oriented Quasi-Atomic Orbitals



a) $O_3o_6\sigma$ (1.96,1.42)

b) $O_3h_1\sigma$ (1.37, 0.63)

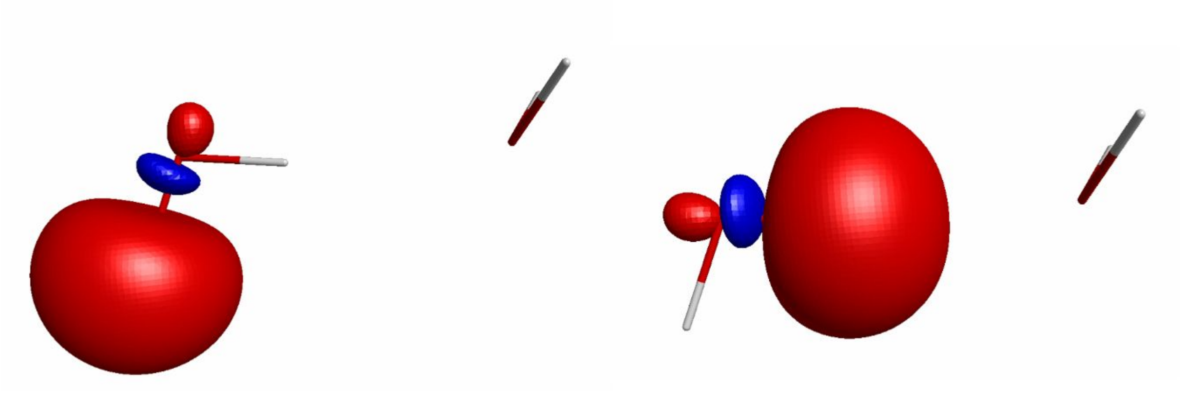
c) H_2o_6h (0.61, 1.97)

d) O_6lp (1.97)

e) $O_3h_2\sigma$ (1.42, 0.61)

Figure 3. Qualitatively unique QUAOs for bonding interactions in the water dimer. The bond label and occupations for each QUAO are shown below the respective figure. The atom numbering system is shown in Figure 2a) QUAOs involved in oxygen-oxygen interaction, b) QUAOs involved in OHσ(o) bond, c) QUAOs involved in a hydrogen bond, d) Lone pair QUAO, e) QUAOs involved in a OHσ(i) bond

The QUAOs for unique interactions in the water dimer are presented in Figure 3, along with the respective label and occupations in each of the QUAOs. QUAO occupations correspond to the atoms in the label in the figure. For example, for $O_3h_1\sigma$ in Figure 3b, the occupation on O_3 is 1.37 electrons and that on h_1 is 0.63 electrons. These occupations add up to exactly 2 since they describe a "normal" O-H bond. On the other hand, for a hydrogen bond, such as that in Figure 3c, the occupations add up to more than 2 since a hydrogen bond is the interaction of a lone pair whose occupation is nearly 2 with a hydrogen atom that participates in a polar O-H bond that performs as the H-donor. The hydrogen bond is a three-center interaction. Based on the occupations shown in Figures 3(a) and 3(c), the occupations for the interaction add up to 4 electrons (1.**42** on O3 + 0.61 on H2 + 1.97 on O6). Occupations for all QUAOs are shown in Table 1, together with the quantitative BO and KBO information. The QUAOs are visually equivalent for the corresponding interactions in the trimer, tetramer, pentamer, and the hexamer family of structures. The colors of the QUAOs represent positive (red) and negative (blue) phases**.** The QUAOS in Figure 3 account for intermolecular interactions (Figure 3a and 3c), and intramolecular interactions (Figure 3b and 3e). By visual inspection, the hydrogen QUAO is more spherical in the OHσ(o) bond than in the OHσ(i) bond. Figure 4a shows the QUAO on the hydrogen involved in the OHσ(o) bond, and Figure 4b shows the QUAO on the hydrogen involved in the OHσ(i) bond. The QUAO shown in Figure 4b can be seen to be slightly deformed when compared to the one shown in Figure 4a. The difference in shape may be attributed to the interaction of the hydrogen QUAO from the OHσ(i) bond with the oxygen lone pair QUAO in the second water molecule.



a) QUAO on H1 b) QUAO on H2

Figure 4. QUAO on the H1 and H2 atoms

The BOs, KBOs, and orbital occupations (occ) for all interacting QUAOs for the dimer, trimer, tetramer and pentamer are shown in Table 1. Also included in Table 1 are the interatomic distances R for all interacting atom pairs. For all systems, the magnitudes of the BOs have the following trends: interactions with BO > 0.90 correspond to OHσ(o) bonds, interactions with BOs between 0.80 and 0.90 correspond to OHσ(i) bonds, and interactions with BOs ≤ 0.30 correspond to hydrogen bonds. The KBOs for all interactions are negative, indicating that all the interactions shown in Table 1 are bonding interactions. Only unique interactions are shown; symmetrically equivalent interactions are omitted.

Table 1. Bond orders, KBOs (kcal/mol), bond lengths R (Å), and orbital occupations for all O-H interactions in the water dimer, trimer, tetramer, and pentamer. Occ(H) and Occ(O) give the occupations of the QUAO centered on H and O, respectively. Type H indicates a hydrogen bond. The KBO in parentheses is the sum of the H-bond and O---O KBOs. Type *lp* indicates a lone pair QUAO, for which distances and hydrogen occupation numbers are omitted. Atom numbering system is given in Figure 2. O* represents all of the oxygen lone pair QUAOs (equivalent by symmetry).

System	BO	KBO	R	Occ(H)	Occ(O)	Bond	Type
Dimer	0.90	-50.3	0.969	0.61	1.42	$H_2 O_3$	σ(i)
	0.92	-48.3	0.962	0.61	1.39	$H_4 O_6$	σ(o)
	0.93	-48.3	0.960	0.63	1.37	$H_1 O_3$	σ(o)
	0.22	-5.9 (-8.3)	1.945	0.61	1.97	$H_2 O_6$	*H*
	-	-	-	-	1.97	O_6	*lp*
Trimer	0.89	-49.7	0.975	0.60	1.43	$H_8 O_7$	σ(i)
	0.89	-49.7	0.975	0.61	1.44	$H_6 O_4$	σ(i)
	0.89	-49.5	0.974	0.60	1.43	$H_2 O_1$	σ(i)
	0.93	-48.8	0.961	0.62	1.38	$H_3 O_1$	σ(o)
	0.93	-48.7	0.960	0.62	1.38	$H_9 O_7$	σ(o)
	0.24	-6.4 (-9.0)	1.89	0.61	1.96	$H_6 O_7$	*H*
	0.24	-6.3 (-8.8)	1.89	0.60	1.96	$H_8 O_1$	*H*
	0.23	-5.9 (-8.3)	1.91	0.60	1.96	$H_2 O_4$	*H*
	-	-	-	-	1.96	O*	*Lp*
Tetramer	0.87	-50.2	0.981	0.60	1.46	$H_3 O_1$	σ(i)
	0.93	-48.8	0.961	0.62	1.38	$H_9 O_7$	σ(o)
	0.29	-9.6 (-13.3)	1.765	0.60	1.94	$H_8 O_1$	*H*
	-	-	-	-	1.94	O*	*Lp*
Pentamer	0.86	-50.4	0.981	0.60	1.47	$H_5 O_4$	σ(i)
	0.93	-49.0	0.961	0.63	1.37	$H_{14} O_{13}$	σ(o)
	0.93	-48.9	0.961	0.63	1.37	$H_{11} O_{10}$	σ(o)
	0.93	-48.9	0.961	0.62	1.38	$H_3 O_1$	σ(o)
	0.93	-48.8	0.961	0.62	1.38	$H_6 O_4$	σ(o)
	0.93	-48.8	0.961	0.62	1.38	$H_9 O_7$	σ(o)
	0.31	-10.6 (-14.6)	1.731	0.60	1.93	$H_2 O_4$	*H*
	0.31	-10.5 (-14.5)	1.731	0.60	1.93	$H_{15} O_7$	*H*
	0.31	-10.5 (-14.5)	1.731	0.60	1.93	$H_8 O_1$	*H*
	0.31	-10.5 (-14.5)	1.731	0.60	1.93	$H_5 O_{10}$	*H*
	0.30	-10.1 (-14.0)	1747	0.60	1.93	$H_{12} O_{13}$	*H*
	-	-	-	-	1.93	O*	*Lp*

OHσ(o) interactions

The OHσ(o) bonds across the clusters consistently have a BO of ~0.92. The KBO values become slightly more negative as the size of the water cluster increases, peaking at -49.0 kcal/mol in the water pentamer ($O_{13}h_{14}\sigma$). Within each water cluster, the KBOs vary only slightly, indicating that the bonds that do not participate in hydrogen bonding are roughly equivalent to each other in each cluster. Bond lengths among the OHσ(o) bonds in the water clusters are in the range 0.960 Å - 0.962 Å. Occupations of the respective QUAOS on the hydrogen and oxygen atoms involved in the OHσ(o) interactions are consistently between 0.60 and 0.63 on the hydrogen, and 1.37 or 1.38 on the oxygen in every system. This indicates a transfer of ~0.38 e- from H to the bonding QUAO on O.

OHσ(i) interactions

The hydrogen atom participating in an OHσ(i) bond forms a hydrogen bond to a second oxygen atom. Experimentally, when a hydrogen bond forms, the OHσ bond stretches, resulting in a lower vibrational frequency and a lower energy of the OHσ bond(6). The longer bond lengths and lower BOs of the OHσ(i) bonds compared to the OHσ(o) bonds, as shown in Table 1, are consistent with these experimental observations. Additionally, the vibrational analysis done on the water clusters to determine if each structure is a minimum on the PES yields lower O-H stretching frequencies for OHσ(i) bonds than for OHσ(o) bonds. However, the KBOs of the OHσ(i) bonds are consistently *slightly* (~1-2 kcal/mol) more negative than the KBOs of the OHσ(o) bonds, implying stronger OHσ(i) bonds. For example, the $O_3h_2\sigma$ bond in the water dimer has a KBO of -50.3 kcal/mol, while the $O_6h_4\sigma$ bond in the same system has a KBO of -48.3 kcal/mol. The analogous trend is found in every water cluster, including the water hexamers discussed in Section 3.2. So, the KBOs for OH bonds that participate in hydrogen bonds compared those that do not are opposite to the trend one would expect. There are multiple possible reasons for the observed trend in KBOs. It may be that KBOs obtained at the HF level of theory are not sufficiently accurate to capture quantitative differences of 1 kcal/mol. In addition, it is possible that non-covalent interactions, such as electrostatics or dispersion, play a role in the relative bonding motifs of OHσ(i) vs. OHσ(o) that are not captured in the predominantly covalent KBOs. It may also be that vibrational frequencies and bond distances do not necessarily reflect subtle differences in bond energies.

As may be seen in Table 1, the occupations of the oxygen QUAOs involved in OHσ(i) bonds are consistently slightly higher than the occupations of the oxygen QUAOs that form OHσ(o) bonds in all clusters by up to 0.07 e-. The difference in occupation is attributed to the charge transfer from the hydrogen atom involved in the hydrogen bond to the respective oxygen. Occupations for the oxygen QUAO range from 1.42 to 1.45, while all of the hydrogen QUAOs have an occupation of ~0.60. The occupations on the H QUAOs that participate in the OHσ(i) bonds are consistently lower than the occupations of the H QUAOs which are not involved in hydrogen bonding due to the interactions of this hydrogen with a second oxygen.

Oxygen-Oxygen Interactions

Oxygen-oxygen interactions are also thought to be important in O-H---O hydrogen bonds(59,60). The O-O interactions for the dimer through the pentamer are displayed in Table 2.

The labels O_1 and O_2 refer to the respective oxygen atoms involved in the interaction. For simplicity, O_1 will represent the hydrogen donor and O_2 the hydrogen acceptor in the hydrogen bonding.

Table 2. Bond orders, KBOs (kcal/mol), distances R (Å), and orbital occupations for all symmetrically significant O-O interactions in the water clusters. Occ(O_1) and Occ(O_2) give the occupations of the QUAOs centered on O_1 and O_2, respectively, with O_1 being the hydrogen donor atom.

	BO	KBO	R	Occ(O_1)	Occ(O_2)	Atoms
Dimer	0.14	-2.4	2.91	1.42	1.96	O_3 O_6
Trimer	0.15	-2.6	2.79	1.44	1.96	O_4 O_7
	0.15	-2.5	2.79	1.44	1.96	O_7 O_1
	0.15	-2.4	2.79	1.43	1.96	O_1 O_4
Tetramer	0.18	-3.7	2.73	1.46	1.94	O_4 O_1
Pentamer	0.19	-4.0	2.71	1.47	1.93	O_4 O_1
	0.19	-4.0	2.71	1.47	1.93	O_1 O_7
	0.19	-4.0	2.72	1.47	1.93	O_7 O_{13}
	0.19	-4.0	2.72	1.47	1.93	O_{10} O_4
	0.18	-3.9	2.73	1.47	1.94	O_{13} O_{10}

Significant oxygen-oxygen bonding interactions exist only between the oxygen orbital that forms an OHσ(i) bond and the oxygen lone pair orbital that participates in the hydrogen bond. These O-O separations (1.7 – 1.9Å) are consistent with the standard definition of the hydrogen bond(59). The KBOs of the interactions are all negative, indicating bonding interactions. Furthermore, as the magnitudes of the BO increases, the KBO consistently becomes more negative indicating a stronger bonding interaction. The BOs and KBOs also steadily increase in magnitude with the size of the water cluster. To analyze the contribution of the O-O interaction to the overall hydrogen bonding interaction energy, the O-O KBOs have been added to the respective H-bond KBOs; the resulting quantities are given in parentheses in Table 1 for each H-bond. The KBO of the O-O interaction strengthens the H-bond *i.e.* a more negative KBO is produced. It is reasonable to include this KBO to form a composite H-bond KBO because hydrogen bonds are three center four electron interactions. Analysis of the O-O interaction in the water dimer reveals that the occupations of the H donor (O_6) and the H acceptor (O_3) QUAOs are 1.42 and 1.96, respectively. The occupation of the hydrogen in this O_6-H_2---O_3 hydrogen bond is 0.61. Summing these three occupations to obtain 3.99 electrons illustrates the characterization of hydrogen bonds as three-center, 4-electron bonds(61–63).

Hydrogen Bonds

Hydrogen bonding is the interaction that holds the water clusters together. The average KBOs and BOs of the hydrogen bonds (labelled *H* in Table 1) in each cluster are displayed in Table 3.

Table 3. Average kinetic bond order (kcal/mol) and average bond order of hydrogen bonds in the water dimer, trimer, tetramer, and pentamer

	Dimer	Trimer	Tetramer	Pentamer
KBO	-5.85	-6.19	-9.6	-10.4
BO	0.22	0.24	0.29	0.31

As the size of the water cluster increases, the average KBO of the hydrogen bonds becomes more negative and the average magnitude of the BO increases, indicating that the strength of a hydrogen bond increases with the number of water molecules in the cluster. This is likely to be related to cooperativity effects as has been noted by Xantheas and co-workers(5). The strongest hydrogen bonds are seen in the water pentamer, in which the KBO values for the hydrogen bonds are all more negative than -10.0 kcal/mol. This is also reflected in the shortening of the corresponding O-H distance of the hydrogen bond. For example, the KBO of the hydrogen bond H_2o_3h in the dimer is -5.9 kcal/mol, with a corresponding O_3H_2 distance of 1.945 Å, while the KBO for the similar hydrogen bond in the trimer H_6o_4h is -6.4 kcal/mol and the distance decreases to 1.89 Å. Each molecule in the water trimer, tetramer, and pentamer has only one OHσ(i) bond (donor) and only one *H* bond (acceptor), resulting in a cyclic structure with a clear direction of the hydrogen bonds, as illustrated in Figure 5. The cyclic geometry and the direction of the hydrogen bonds allows them to engage in a cooperative effect to stabilize the geometry and strengthen the hydrogen bond network as more water molecules are included. The numbers shown in Table 3 follow the expected trend of BOs and KBOs: as the BOs increase, the KBOs show a stronger bond. The hexamer isomers are more complicated and are discussed below.

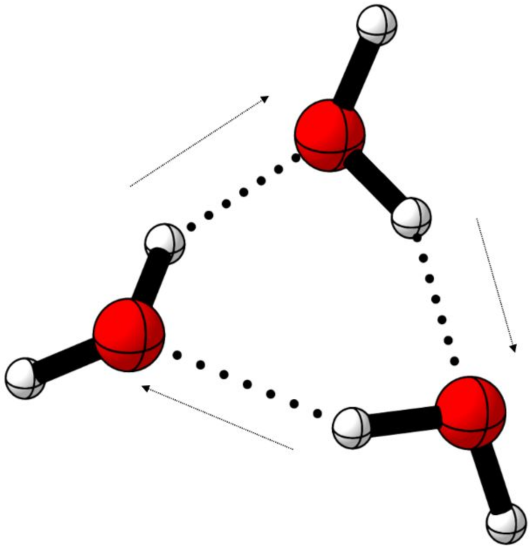


Figure 5. Direction of the hydrogen bonds in the water trimer

Hexamers

The six lowest energy water hexamers, based on many previous reports(7,64,65), referred to as the cyclic, book, bag, prism, boat and cage, are illustrated in Figure 6. These six previously determined(7) water hexamer configurations are analyzed in the present study. The hexamer configurations may be separated into three groups. The oxygens in the highly symmetric cyclic and boat isomers are almost planar and do not have any double donors or double acceptors. The bag and book conformations are the first to show a homodromic network arrangement: both have a single water molecule acting as a double donor and bag has a different water molecule acting as a double acceptor as well. In the bag conformation, the oxygen labeled O_4 acts as a double donor producing the hydrogen bonds H_5o_7h and $H_6o_{16}h$. Furthermore, the water molecule that contains O_{13} is a double acceptor for the hydrogen bonds $H_9o_{13}h$ and $H_{18}o_{13}h$. In the book conformation, the oxygen labeled O_{10} acts as a double donor, while the water molecule that contains O_{16} is a double acceptor. Finally, the prism and cage hexamers have the most complex geometries with multiple water molecules that act as either double acceptors or double donors (examples are O_4 and O_{10} in the prism, and O_7 and O_{13} in the cage as double donors; O_1 and O_{16} in the prism, and O_1 and O_{10} in the cage as double acceptors). In the latter four isomers, one can also identify O_x-H---O_y hydrogen bonds in which O_x is a double acceptor. These are referred to as (had) in the following discussion.

The presence of double acceptors and double donors make the water hexamers very interesting systems, in which the oxygen atoms are no longer all coplanar, in contrast to the smaller water clusters. The electronic effects that arise from the cooperative and anti-cooperative contributions, which vary according to the nature of the hydrogen and σ bonds, are reflected by the BOs and KBOs. Analysis of the QUAOs provides insight into the nature of the electronic effects that stabilize the hexamer geometries. The BOs, KBOs, and orbital occupations are summarized in Tables 4 through 9.

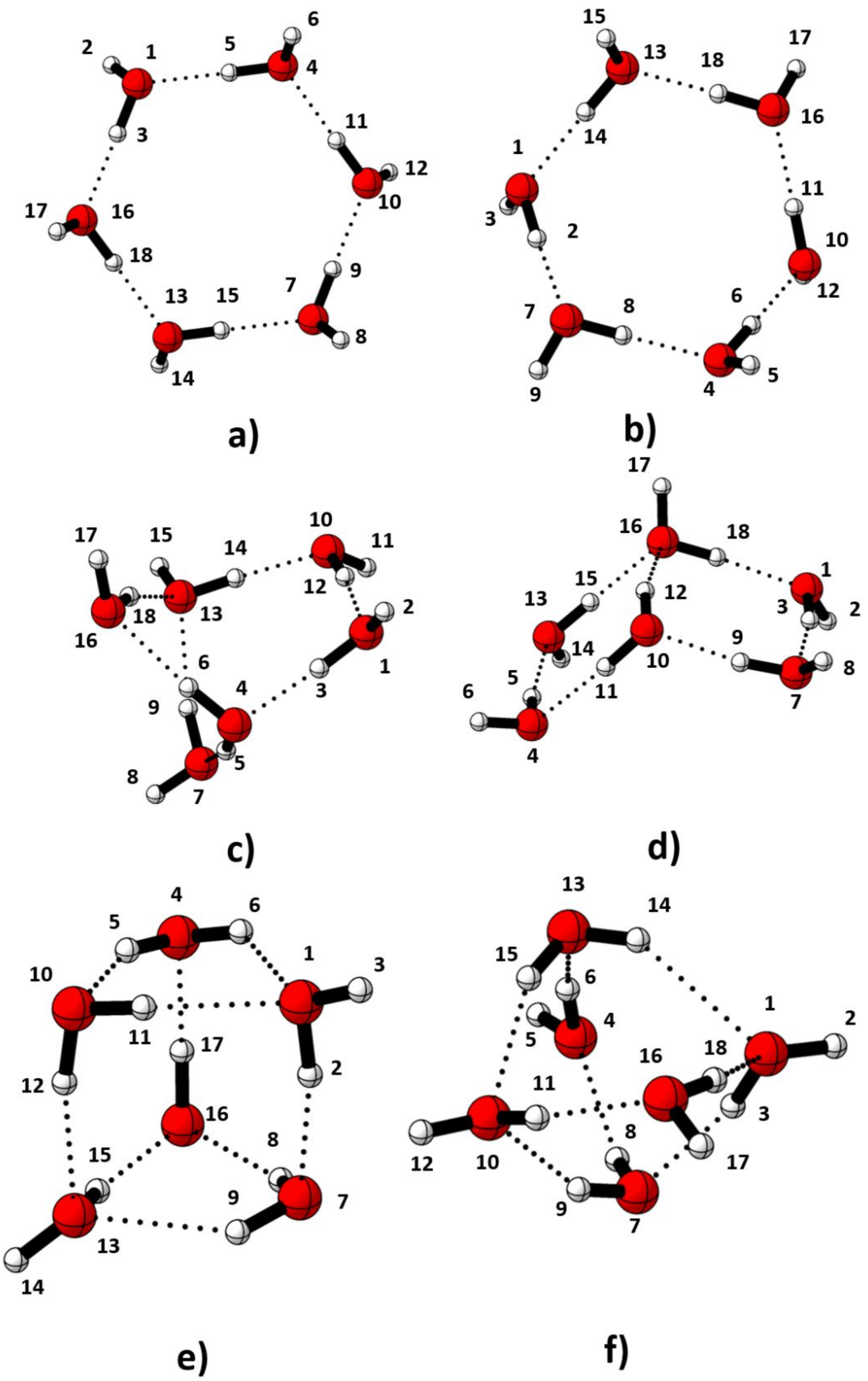


Figure 6. Geometry of the water hexamers: a) Cyclic b) Boat; c) Bag; d) Book; e) Prism; f) Cage

Table 4. Bond orders, KBOs (kcal/mol), bond lengths R (Å), and orbital occupations for all O-H interactions in the cyclic conformation of the water hexamers. Occ(H) and Occ(O) give the occupation of the QUAO centered on H and O, respectively. Type H indicates a hydrogen bond. Only the unique significant contributions are shown.

Cyclic

Type	BO	KBO	R	Occ(H)	Occ(O)	Bond
σ(i)	0.86	-50.2	0.984	0.60	1.47	H_{15} O_{13}
σ(o)	0.93	-48.5	0.961	0.62	1.38	H_6 O_4
H	0.31	-10.9 (-15.01)	1.718	0.60	1.93	H_{11} O_4

Table 5. Bond orders, KBOs (kcal/mol), bond lengths R (Å), and orbital occupations for all O-H interactions in the boat conformations of the water hexamer. Occ(H) and Occ(O) give the occupation of the QUAO centered on H and O, respectively. Type H indicates a hydrogen bond.

Boat

Type	BO	KBO	R	Occ(H)	Occ(O)	Bond
σ(i)	0.86	-50.5	0.983	0.60	1.47	H_6 O_4
	0.86	-50.4	0.984	0.60	1.47	H_8 O_7
	0.86	-50.4	0.984	0.60	1.47	H_{18} O_{16}
σ(o)	0.93	-49.0	0.960	0.63	1.38	H_3 O_1
	0.93	-49.0	0.960	0.63	1.38	H_{12} O_{10}
	0.93	-48.9	0.961	0.63	1.37	H_5 O_4
	0.93	-48.9	0.951	0.63	1.37	H_{15} O_{13}
	0.93	-48.8	0.961	0.62	1.38	H_9 O_7
	0.93	-48.8	0.961	0.62	1.38	H_{17} O_{16}
H	0.31	-10.8 (-14.9)	1.722	0.60	1.93	H_2 O_7
	0.31	-10.7 (-14.8)	1.724	0.60	1.93	H_8 O_4
	0.30	-10.5 (-14.5)	1.726	0.60	1.93	H_6 O_{10}

Table 6. Bond orders, KBOs (kcal/mol), bond lengths R (Å), and orbital occupations for all O-H interactions in the bag conformations of the water hexamer. Occ(H) and Occ(O) give the occupation of the QUAO centered on H and O, respectively. Type H indicates a hydrogen bond. dd indicates a bond produced by a double donor, da indicates a bond produced by a double acceptor, had indicates a hydrogen bond O_x-H---O_y in which O_x is a double acceptor

			Bag			
Type	BO	KBO	R	Occ(H)	Occ(O)	Bond
σ(i)	0.88	-50.5	0.975	0.61	1.44	H_{18} O_{16}
	0.89	-50.5	0.974	0.61	1.43	H_9 O_7
	0.89	-50.3	0.974	0.61	1.43	H_6 O_4
	0.89	-50.2	0.974	0.61	1.43	H_5 O_4
	0.85	-50.1	0.993	0.60	1.49	H_{14} O_{13}
	0.85	-50.1	0.989	0.59	1.48	H_{12} O_{10}
	0.85	-49.9	0.991	0.60	1.48	H_3 O_1
σ(o)	0.92	-49.3	0.962	0.62	1.38	H_{15} O_{13}
	0.93	-49.1	0.960	0.62	1.38	H_2 O_1
	0.93	-48.8	0.961	0.63	1.37	H_{17} O_{16}
	0.92	-48.8	0.961	0.62	1.38	H_{11} O_{10}
	0.93	-48.7	0.961	0.62	1.38	H_8 O_7
H	0.34	-12.5 (-17.1)	1.670	0.60	1.92	H_{14} O_{10} had
	0.34	-12.1 (-16.5)	1.686	0.60	1.92	H_3 O_4
	0.32	-11.6 (-15.9)	1.687	0.59	1.92	H_{12} O_1
	0.26	-7.5 (-10.5)	1.850	0.61	1.95	H_{18} O_{13} da
	0.24	-6.8 (-9.5)	1.885	0.61	1.96	H_9 O_{13} da
	0.24	-6.8 (-9.6)	1.895	0.61	1.96	H_5 O_7 dd
	0.24	-6.6 (-9.3)	1.893	0.61	1.96	H_6 O_{16} dd

Table 7. Bond orders, KBOs (kcal/mol), bond lengths R (Å), and orbital occupations for all O-H interactions in the book conformations of the water hexamer. Occ(H) and Occ(O) give the occupation of the QUAO centered on H and O, respectively. Type H indicates a hydrogen bond. dd symbolizes a bond produced by a double donor, da indicates a bond produced by a double acceptor, had indicates a hydrogen bond O_x-H---O_y in which O_x is a double acceptor

Book

Type	BO	KBO	R	Occ(H)	Occ(O)	Bond
σ(i)	0.88	-50.7	0.977	0.60	1.45	H_{15} O_{13}
	0.90	-50.5	0.969	0.62	1.41	H_{12} O_{10}
	0.88	-50.5	0.977	0.60	1.45	H_{11} O_{10}
	0.85	-50.4	0.989	0.60	1.48	H_{18} O_{16}
	0.88	-50.4	0.978	0.61	1.45	H_5 O_4
	0.86	-50.0	0.988	0.60	1.48	H_3 O_1
	0.86	-49.8	0.989	0.60	1.48	H_9 O_7
σ(o)	0.92	-49.1	0.961	0.62	1.38	H_{17} O_{16}
	0.93	-49.0	0.961	0.62	1.38	H_8 O_7
	0.92	-48.9	0.961	0.62	1.38	H_2 O_1
	0.93	-48.8	0.961	0.62	1.38	H_{14} O_{13}
	0.93	-48.8	0.961	0.63	1.37	H_6 O_4
H	0.32	-11.6 (-15.9)	1.693	0.60	1.92	H_{18} O_1 had
	0.32	-11.3 (-15.5)	1.707	0.60	1.93	H_9 O_{10}
	0.32	-11.1 (-15.3)	1.707	0.60	1.93	H_3 O_7
	0.27	-8.7 (-12.1)	1.801	0.61	1.95	H_5 O_{13}
	0.27	-8.5 (-11.9)	1.805	0.60	1.95	H_{15} O_{16} da
	0.27	-8.1 (-11.4)	1.827	0.60	1.95	H_{11} O_4 dd
	0.21	-4.9 (-7.0)	1.992	0.62	1.97	H_{12} O_{16} dd, da

Table 8. Bond orders, KBOs (kcal/mol), bond lengths R (Å), and orbital occupations for all O-H interactions in the prism conformations of the water hexamer. Occ(H) and Occ(O) give the occupation of the QUAO centered on H and O, respectively. Type H indicates a hydrogen bond. dd symbolizes a bond produced by a double donor, da indicates a bond produced by a double acceptor, had indicates a hydrogen bond O_x-H---O_y in which O_x is a double acceptor

Prism

Type	BO	KBO	R	Occ(H)	Occ(O)	Bond
σ(i)	0.90	-50.0	0.971	0.62	1.42	$H_{12}O_{10}$
	0.87	-49.9	0.983	0.60	1.46	H_2O_1
	0.88	-49.8	0.977	0.60	1.44	$H_{15}O_{13}$
	0.89	-49.5	0.971	0.61	1.43	H_8O_7
	0.85	-49.3	0.996	0.60	1.49	$H_{17}O_{16}$
	0.90	-49.2	0.970	0.62	1.41	$H_{11}O_{10}$
	0.88	-49.1	0.981	0.60	1.45	H_5O_4
	0.91	-48.8	0.967	0.61	1.41	H_9O_7
	0.90	-48.8	0.968	0.61	1.41	H_6O_4
σ(o)	0.92	-49.1	0.961	0.62	1.38	$H_{18}O_{16}$
	0.92	-48.8	0.961	0.62	1.38	H_3O_1
	0.92	-48.7	0.961	0.62	1.38	$H_{14}O_{13}$
H	0.35	-12.8 (-17.4)	1.662	0.60	1.91	$H_{17}O_4$ had
	0.30	-9.8 (-13.8)	1.763	0.60	1.93	H_2O_7 had
	0.27	-7.8(-10.8)	1.847	0.60	1.95	H_5O_{10} dd
	0.26	-7.5 (-10.5)	1.841	0.60	1.95	$H_{15}O_{16}$ da, had
	0.22	-5.7 (-8.1)	1.959	0.62	1.96	$H_{12}O_{13}$ dd, da
	0.21	-5.0 (-7.1)	1.970	0.61	1.97	H_8O_{16} da
	0.19	-4.3 (-6.1)	2.045	0.62	1.97	$H_{11}O_1$ da, dd
	0.16	-3.0 (-4.3)	2.148	0.61	1.98	H_6O_1 dd, da
	0.15	-2.6 (-3.7)	2.177	0.61	1.98	H_9O_{13} da

Table 9. Bond orders, KBOs (kcal/mol), bond lengths R (Å), and orbital occupations for all O-H interactions in the cage conformations of the water hexamer. Occ(H) and Occ(O) give the occupation of the QUAO centered on H and O, respectively. Type H indicates a hydrogen bond. dd symbolizes a bond produced by a double donor, da indicates a bond produced by a double acceptor, had indicates a hydrogen bond O_x-H---O_y in which O_x is a double acceptor

Cage

Type	BO	KBO	R	Occ(H)	Occ(O)	Bond
σ(i)	0.87	-49.8	0.983	0.60	1.46	$H_{11}O_{10}$
	0.87	-49.8	0.980	0.60	1.46	$H_{18}O_{16}$
	0.89	-49.8	0.971	0.61	1.42	$H_{15}O_{13}$
	0.88	-49.8	0.977	0.60	1.45	H_8O_7
	0.90	-49.6	0.970	0.61	1.42	H_9O_7
	0.87	-49.6	0.982	0.60	1.46	H_6O_4
	0.85	-49.4	0.994	0.60	1.48	H_3O_1
	0.90	-49.2	0.969	0.61	1.41	$H_{14}O_{13}$
σ(o)	0.92	-49.0	0.961	0.62	1.38	H_2O_1
	0.92	-48.9	0.961	0.62	1.38	$H_{12}O_{10}$
	0.92	-48.8	0.960	0.62	1.38	H_5O_4
	0.92	-48.5	0.961	0.62	1.38	$H_{17}O_{16}$
H	0.34	-11.9 (-16.2)	1.688	0.60	1.95	H_3O_7 had
	0.30	-9.6 (-13.3)	1.757	0.60	1.96	$H_{11}O_{16}$ had
	0.29	-9.1 (-12.6)	1.789	0.60	1.96	H_6O_{13}
	0.28	-8.7 (-12.1)	1.789	0.60	1.96	$H_{18}O_1$ da
	0.26	-7.5 (-10.5)	1.829	0.60	1.97	H_8O_4 dd
	0.22	-5.5 (-7.8)	1.967	0.61	1.98	$H_{15}O_{10}$ dd, da
	0.20	-4.7 (-6.7)	2.001	0.61	1.98	H_9O_{10} dd, da
	0.18	-3.9 (-5.6)	2.081	0.61	1.98	$H_{14}O_1$ dd, da

OHσ(o)

The OHσ(o) bonds generally have a higher BO than the OHσ(i) bonds, which is consistent with experimental bond distances and vibrational frequencies. The BOs for the OHσ(o) bonds in the water hexamers range from 0.90 to 0.93. The number of OHσ(o) bonds, double donors, and double acceptors for each conformation are summarized in Table 10. As the number of water molecules acting as either dd or da increases, the number of OHσ(o) bonds decreases, as one would expect.

Table 10. Number of OHσ(o) bonds, double donors (dd) and double acceptors (da) and oxygens acting as double acceptors (had) in the water hexamers

Cluster	# of OHσ(o)	# of (dd)	# of (da)	# of (had)
Boat	6	0	0	0
Cyclic	6	0	0	0
Bag	5	1	1	1
Book	5	1	1	1
Cage	4	2	2	2
Prism	3	2	2	3

The symmetric boat and cyclic conformations have one OHσ(o) bond in each water molecule, resulting in a larger number of OHσ(o) bonds than are in the other isomers. The OHσ(o) bond BOs are consistently ~0.93 in the boat and cyclic conformations, and the corresponding KBOs are in the range 48-49 kcal/mol.

The book and bag conformations each have five OHσ(o) bonds. Figure 4 shows that one water molecule in each conformer acts as a double donor (O_{10}, O_4, respectively), resulting in one less OHσ(o) bond than the cyclic and boat conformers. The KBOs of the OHσ(o) bonds are again ~ -49 kcal/mol.

The prism and cage conformers have the lowest number of OHσ(o) bonds of all of the hexamer conformers studied, three and four, respectively. The BO of all of the OHσ(o) bonds in the prism and cage conformers is 0.92, similar to the BOs of the OHσ(o) bonds in other isomers. Similarly, the KBOs in the prism and cage water hexamers for the OHσ(o) bonds on the order of -49 kcal/mol.

In all of the hexamer conformers, the occupations of the hydrogen QUAOs participating in the OHσ(o) bonds are ~0.62, and the corresponding oxygen QUAO occupations are ~1.38. Thus, aside from a few nuances, the OHσ(o) bonds in the water hexamers are similar among the conformers.

OHσ(i)

The OHσ(i) bonds in the water hexamers have a similar pattern to those in the smaller water clusters. The OHσ(i) bonds have lower BOs than the OHσ(o) bonds, and they are associated with more negative KBOs.

In the cyclic and boat conformations, the OHσ(i) bonds have a BO of 0.86, and the corresponding KBOs are ~50 kcal/mol, about 1 kcal/mol larger than for the OHσ(o) bonds. Indeed, for all water hexamer isomers, the OHσ(i) KBOs are on the order of 50-51 kcal/mol.

Hydrogen Bonds

The total number of H bonds, average H bond KBO, and average H bond BO for each hexamer conformer are listed in Table 11. Additionally, in Tables 4-9, a H bond labelled as (da) originates from an oxygen atom acting as a double acceptor, a (dd) label symbolizes an H bond originating from a double donor, a (had) label symbolizes an O_x-H-O_y hydrogen bond in which O_x is a double acceptor, and no explicit label corresponds to a single donor or single acceptor oxygen H bond.

Table 11. Total number of Hydrogen Bonds (H) and average BO and KBO (kcal/mol) for each water hexamer conformation

	Boat	Cyclic	Bag	Book	Prism	Cage
# H-bonds	**6**	**6**	**7**	**7**	9	8
Average BO	0.28	0.28	0.31	0.31	0.23	0.26

Average KBO[a]	-10.7	-10.9	-9.1 (-12.1)	-9.2 (-10.7)	-6.5 (-11.3)	-7.6 (-10.2)

a. The average KBO excluding dd and da hydrogen bonds in given in parentheses

In the highly symmetric boat and cyclic hexamer isomers, all H bonds have similar BOs and KBOs to one another, with the magnitude of the KBOs in the range of 10.5-11 kcal/mol. So, the average KBO for the cyclic and boat hexamer species is larger in magnitude than the average KBOs for the smaller clusters. These KBOs continue the trend seen in Table 3, which illustrates a systematic increase in hydrogen bonding strength as the size of the cluster increases. This trend continues with the cyclic and boat isomers and illustrates the cooperativity among the hydrogen bonds as the size of the cluster increases.

The situation becomes more complicated for the other four hexamer isomers. There is a larger range of KBOs in the more complex conformers, bag, book, prism, cage, due to the cooperativity and anti-cooperativity effects of the double donors and double acceptors that are present in these structures. Overall, in the latter four isomers, the hydrogen bonds that involve simply single donor/single acceptor interactions, similar to those in the cyclic and boat conformations, have KBO magnitudes in the range 9-12.5 kcal/mol. On the other hand, the hydrogen bonds that involve double donors and/or double acceptors are weaker, with magnitudes below 8 kcal/mol and some even below 4 kcal/mol. This kind of phenomenon has been observed previously in molecules like silatranes(66) and referred to as “sacrificial bonding”. This flowery description suggests that there are only so many electrons (electron density) to go around, and when they are spread over multiple bonds, those bonds become weaker on average. Interestingly, as shown in Tables 6-9, the (had) hydrogen bonds have KBOs that are consistently among the largest in magnitude. For example, $O_4h_{17}h$ is the strongest H bond in the prism conformation and among all the hexamers. This is due to the overall bonding pattern leading to this $O_{16}H_{17}$---O_4 (had) hydrogen bond. The two hydrogen bonds being accepted by O_{16} ($O_{16}h_8h$) and ($O_{16}h_{10}h$) slightly weakens the $O_{16}H_{17}$ bond, as may be confirmed in Table 8. This makes H_{17} more acidic, thus producing a stronger hydrogen bond(28,36). A similar pattern is observed for nearly all of the had bonds.

Conclusions:

The bonding analysis of water clusters with the QUAO methodology has provided insight into the nature of the sigma and hydrogen bonding interactions in the different water clusters studied. It has been shown that the symmetry and geometry of the water clusters, and the presence of homodromic networks in the structure have a direct impact on the strength of the bonding interactions. Weaker hydrogen bonds are found when double acceptors or double donors are present, due to anti-cooperativity effects. The distribution of H bond KBOs is greater for the bag, book, prism and cage hexamers due to the presence of double donors and double acceptors. Due to cooperativity effects, the overall trend in hydrogen bond KBOs is a systematic increase in magnitude with the size of the cluster, from dimer to those hexamers that contain no double donor or double acceptor hydrogen bonds. There is little variation in the KBOs for these species. The presence of double donor and double acceptor hydrogen bonds, especially in the prism and cage isomers, tends to cause a wider set of variations in the KBO values and to reduce the overall magnitude of the H-bond KBOs in these species relative to the other four isomers. In particular, hydrogen bonds O_x-H---O_y, in which O_x is a double acceptor, referred to as had bonds, are generally stronger, due to increased acidity in the hydrogen H_x atom. Conversely, hydrogen bonds that involve double donors or double acceptors are generally among the weakest using the KBOs as a metric, due to sacrificial bonding.

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