

## **A Cooperative Calculation of Geometries, Energetics and Electric Properties of Water Trimers and Tetramers**

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The cooperative model of Campbell and Mezei reproduces Kistenmacher, Lie, Popkie and Clementi's Hartree-Fock energy for  $(\text{H}_2\text{O})_4$  with only a 3% error. Permanent multipole electric fields at the O nuclei and induced dipole vectors have been calculated. Analysis of a redetermination of the geometry of  $(\text{H}_2\text{O})_4$  suggests the probable symmetry of the structure at the energy minimum. The non-additive and the cooperative energies (defined below) are reported. A non-cooperative calculation of the non-additivity introduces a substantial error.

**Key words:** Cooperativity – Non-additivity – Induced moments – Water energies – Water geometries.

### **1. Introduction**

This paper reports the successful test of the cooperative model of Campbell and Mezei [1] in the calculation of the Hartree-Fock energy for the water tetramer at the energy minimum [2]. Analysis of the results suggests the probable symmetry of the configuration at the absolute minimum. The induced dipole-vectors, electric-fields, cooperativity and non-additivity have been calculated for both the trimer and tetramer of minimum Hartree-Fock energy [2]. (The cooperativity is defined as the energy arising from that part of the dipole vector at a given site which is induced by the electric field defined by the induced dipole-vectors of all other molecules.)

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In this model the interaction energy of  $n$  molecules is

$$U(n) = U_p(n) + U_i(n) + U_r(n) + U_d(n), \quad (1)$$

where  $U_p(n)$  is the first order Coulomb energy,  $U_i(n)$  is the energy contribution involving induced multipoles,  $U_r(n)$  is a repulsion contribution and  $U_d(n)$  is a dispersion contribution, which vanishes in the Hartree–Fock approximation. All applications which have been made thus far have used the following additional approximations.  $U_p$  is approximated by a high order permanent multipole expansion,  $U_i$  includes only the induced dipole vectors and these are calculated from equations which include only terms in the energy quadratic in the electric field components evaluated at the oxygen nuclei and which neglect all terms in their derivatives [3, 4]. Since the value of the electric field vector at a given center is given by sum of the electric fields defined by all other centers, the energy involving induced dipole vectors is non-additive even in the non-cooperative approximation when the contribution of the induced dipole vector to the electric field at other molecules is neglected and only the permanent multipole fields are included. The non-additive contribution to  $U$ , has been neglected and the previous model [1] with inverse ninth and twelfth powers at the atomic nuclei has been used. This model has been shown (i) to reproduce [1] (a) the 229 Hartree–Fock dimer energies [2] somewhat better than that of an alternative analytical fit [2, 5] and (b) the minimum Hartree–Fock trimer energy [2] with an error of 1.3%; (ii) to give a useful first order approximation to the non-additive contribution of other trimers [6] as well [1]. With the inclusion of different approximations for the dispersion contribution the model has been used to calculate the lattice energy of rotationally disordered ice Ih and the rotationally ordered ices II and IX [7]. The validity of the multipole approximation for such calculations on water has been studied [7]. Recently the Hartree–Fock energies and their non-additive components have been reported for twenty-eight additional trimers and the non-additivities compared with non-additivities for the induction contribution based on approximate bond-polarizabilities and point charge models [8]. The approximate agreement of the two was combined with qualitative arguments to draw the same conclusion inferred from the earlier evidence summarized above and the results reported in this paper: the induction contribution provides the major part of the non-additive contribution.

## 2. The Energy Surface for the Tetramer in an Additive Approximation

All calculations were performed for the molecular geometry [9], also used for previous studies [1, 7]:

$$\langle x, y, z \rangle = \{ \text{O: } \langle 0, 0, 0 \rangle; \text{H: } \langle -1.102\ 8459, \pm 1.453\ 7993, 0 \rangle \text{ a.u.,} \\ 1 \text{ a.u.} = 0.529\ 167 \text{ \AA} \}. \quad (2)$$

Since only the approximate hydrogen-bonded directions were reported and the orientations of the non-bonded OH were not specified, the same analytical fit with the revised set of parameters [2] was used to redetermine the minimum

**Table 1.** Analytical fit energies in a.u. for the minimal energy trimer

	I (original)	II (revised)	III (published)
Dimer (1, 2)	$-6.83\ 432 \times 10^{-3}$	$-6.48\ 719 \times 10^{-3}$	$-6.66 \times 10^{-3}$
Dimer (1, 3)	$-6.69\ 804 \times 10^{-3}$	$-6.40\ 524 \times 10^{-3}$	$-6.68 \times 10^{-3}$
Dimer (2, 3)	$-7.03\ 409 \times 10^{-3}$	$-6.70\ 817 \times 10^{-3}$	$-6.29 \times 10^{-3}$
Trimer	$-2.05\ 665 \times 10^{-2}$	$-1.96\ 006 \times 10^{-2}$	$-1.96 \times 10^{-2}$

I(II) give our values calculated using the original [5] (revised [2]) parameters. Column III gives the published energies [2]. The O coordinates of the molecules are: (1) (0, 0, 0); (2) (5.5946, 0, 0); (3) (2.8132, -4.8504, 0) a.u.

energy configuration. However, the following comparisons suggest that the parameters used in the previous determination differed somewhat from either the original or revised published values. For the trimer for which all atomic positions were specified, Table 1 shows that we obtained different dimer energies, although the trimer energy for the revised values agrees with the reported value to the published number of digits.

Since a previous study of the tetramer [2] placed the O atoms at the corners of a square, it seems likely that the configuration at the absolute energy minimum should possess a symmetry with respect to the OH bonds of the different molecules and that the reported deviation from symmetry was probably a consequence of the points sampled in the previous optimization scheme. In this work a square configuration of the O atoms was assumed and the following sequence of optimizations was followed starting from the O-O distance and from H-bond directions within the range given by the previous study:

- (1) the orientations of the non H-bonded OH with the H-bonded OH as rotation axes;
- (2) the O-O distance in the square;
- (3) the H-bond directions varied by rotations about three independent axes (the  $O_{\text{donor}} \rightarrow O_{\text{acceptor}}$  axis, the perpendicular to the molecular plane and their cross product);
- (4) the non H-bonded OH with the H-bonded OH as rotation axes. The computational requirement is illustrated by the  $\sim 200$  sec central processor time required for each set of  $9^4$  orientations of the H-bond directions. This gave  $d_{0-0} = 5.58\ 237$  a.u. (compared with the published value  $2.95\ \text{\AA}$  (5.575 a.u.) [2]). The atomic coordinates are given in Table 2 and angular coordinates to show the

**Table 2.** Atomic coordinates in a.u. for the minimal energy tetramer

Molecule	0	O → HB	O → NHB
1	(0, 0, 0)	(1.7814, 0.3114, -0.0412)	(-0.6466, 1.1649, 1.2235)
2	(5.5824, 0, 0)	(0.2997, -1.7836, 0.0287)	(1.1852, 0.6505, -1.2017)
3	(5.5824, -5.5824, 0)	(-1.7814, -0.3114, -0.0412)	(0.6466, -1.1649, 1.2235)
4	(0, -5.5824, 0)	(-0.2997, 1.7836, 0.0287)	(-1.1852, -0.6505, -1.2017)

HB designates the H-bonded H and NHB the non H-bonded H. Molecule (i) is a donor to molecule (i + 1). 1 a.u./molecule =  $2.6254\ 998 \times 10^6$  -J/mol.

**Table 3**

Molecules		$90^\circ - \theta$	$\phi$	$\psi$
1	HB	-1.31	9.92	9.92
2	HB	0.91	350.46	9.54
3	HB	-1.31	189.92	9.92
4	HB	0.91	170.46	9.54
1	NHB	42.56	119.03	119.03
2	NHB	-41.63	118.76	118.76
3	NHB	42.56	299.03	119.03
4	NHB	-41.63	241.24	118.76

The angles in degrees are for the H-bonded (HB) and non H-bonded (NHB) OH directions. The  $Z$  axis is perpendicular to the oxygen plane.  $\theta$  and  $\phi$  are the spherical polar angles and  $\psi$  is the angle between the projection of the OH in the O-plane and the  $O_{\text{donor}} \rightarrow O_{\text{acceptor}}$  vector

symmetry of the structure in Table 3. This structure had an energy of  $-3.255\ 8292 \times 10^{-2}$  a.u.

Since in the course of the minimization, a somewhat asymmetric structure was observed to be replaced by a completely and/or more nearly symmetric structure as the optimization approached closer to the minimum, the results of Table 3 suggest that the angles for the structure at the absolute energy minimum have the form given in Table 4.

This suggestion was confirmed when the energy was found to be slightly lowered [ $9.46 \times 10^{-7}$  a.u. (0.0029%)] by symmetrizing the angles of Table 3 to have the form of Table 4, with

$$\beta = 1.111^\circ, \gamma = 9.729^\circ, \delta = 42.095, \varepsilon = 118.896. \quad (3)$$

Such a pattern, which should extend to other planar polymers  $(\text{H}_2\text{O})_{2n'}$  will be extremely useful in their optimization. The flatness of the energy surface is shown by the following shifts in energy,  $\Delta u$ . When the O-O distance is varied by  $5.57 \pm 0.03$  a.u.,  $|\Delta u| < 2.6 \times 10^{-2}$  a.u. and under  $\pm 4^\circ$  rotations about (the O-O axis, the perpendicular to the molecular plane, their cross product),  $|\Delta u| < (0.0024 \times 10^{-2}, 0.022 \times 10^{-2}, 0.025 \times 10^{-2})$ . For the following reasons it is

**Table 4.** Angles for the tetramer configuration at the absolute minimum

Molecule		1	2	3	4
HB	$90^\circ - \theta$	$-\beta$	$\beta$	$-\beta$	$\beta$
	$\psi$	$\gamma$	$\gamma$	$\gamma$	$\gamma$
NHB	$90^\circ - \theta$	$\delta$	$-\delta$	$\delta$	$-\delta$
	$\psi$	$\varepsilon$	$\varepsilon$	$\varepsilon$	$\varepsilon$

All symbols are defined as in Table 3

unlikely that either the original [5] or revised [2] parameter sets for the analytical fit would give a minimum  $0.014 \times 10^{-2}$  a.u. lower than our value and thus equal to the published value,  $-3.27 \times 10^{-2}$  a.u. [2].

(1) The energy surface about our minimum was searched over a region larger than that defined by the published uncertainty in H-bond positions for configurations leading to an alternative local minimum. No symmetry was assumed. No other lower local minimum was found.

(2) The position of the local minimum we found was determined to a sufficient accuracy that the above flatness of the surface excludes a further decrease in energy of this magnitude.

### 3. Calculations for the Non-Additive Model

The calculations were performed using the molecular geometry of Eq. (2), the wave function of [5] as regenerated by [1], and the polymer geometry of Table 2. The multiple moments and characteristic directions were generated by the procedure of [10].  $U_p$  was calculated by Method IV of [11] in the three-center expansion of [12] including all interactions of orders  $\leq 14$ . The heuristic comparison of multipole sums for successive orders indicated that the permanent multipole sum had converged within  $1 \times 10^{-6}$  a.u. The induced dipole vectors were calculated as the solution of a set of simultaneous linear equations [13] modified for the case of molecules at random sites and  $U_i$  was then computed using the procedure of [14]. The polarizability tensor elements of [15] (see [7] for a comparison with other polarizability values) were used. These calculations gave the model energy  $U(4) = U_p(4) + U_i(4) + U_r(4) = -3.841\ 4675 \times 10^{-2}$  a.u., which agrees well with the Hartree-Fock value  $U_{HF}(4) = -3.724 \times 10^{-2}$  a.u.,  $[(U_{HF}(4) - U(4))/U_{HF}(4)] = 0.0306$ .

In the local frame (2) the induced ( $\vec{\mu}_i$ ) and total dipole vectors ( $\vec{\mu}_t$ ) for the symmetric structure of Table 4 and Eq. (3) are:

$$\begin{aligned}\vec{\mu}_i &= \langle -0.2237, -0.0835, 0.0862 \rangle \text{ a.u.} \\ \vec{\mu}_t &= \langle -1.0882, -0.0835, 0.0862 \rangle \text{ a.u.}\end{aligned}\quad (4)$$

$$\|\vec{\mu}_i\| = 0.2539 \text{ a.u. (0.6454 D)}, \|\vec{\mu}_t\| = 1.0948 \text{ a.u. (2.7827 D)}$$

[2.541 765 Debye/a.u.,  $8.478\ 418 \times 10^{-30}$  C·m/a.u.].

These values of Eq. (4) compare with the average values ( $\|\vec{\mu}_i\| = 0.1167$  a.u.,  $\|\vec{\mu}_t\| = 0.9583$  a.u.) for the optimal dimer and an average value for non-polar configurations of ice Ih [7] ( $\|\vec{\mu}_i\| = 0.5470$  a.u.,  $\|\vec{\mu}_t\| = 1.4115$  a.u.).

The corrections of [7] for the errors in the charge density defined by the particular Hartree-Fock wave function used give as the best estimates:

$$\|\vec{\mu}_i\| = 0.2051 \text{ a.u. (0.5213 D)}, \|\vec{\mu}_t\| = 0.9148 \text{ a.u. (2.3252 D)}.\quad (5)$$

The angles between the induced and permanent dipole vectors and between the total and permanent dipole vectors of Eq. (6) reflect the difference of symmetry

of the various structures:

			Ice Ih [7a]		
	Dimer	Tetramer	Av. Minimum	Av. Maximum	
$\langle(\vec{\mu}_b, \vec{\mu}_i)^0\rangle$	(41.35, 28.29)	21.92	—	—	(6)
$\langle(\vec{\mu}_b, \vec{\mu}_{\text{perm}})^0\rangle$	(4.42, 4.17)	6.29	0.73	3.91	

The permanent multipole electric field at the oxygen nuclei in the local frame given by Eq. (2) is

$$\vec{E} \times 10^2 \text{ a.u.} = \{\text{optimal dimer: } \langle -0.6194, -0.5463, 0 \rangle, \langle -1.0588, 0, -0.76862 \rangle; \text{optimal symmetric tetramer of Table 4 and Eq. (3): } \langle -1.8653, -0.5594, 0.8755 \rangle\}; 1 \text{ a.u.} = 5.142 \text{ } 2500 \times 10^{11} \text{ V m}^{-1}. \quad (7)$$

The non-cooperative approximation,  $U(n, \text{non-coop})$ , to our model is obtained when the contributions of the induced dipole vectors to the electric field at a given molecule are omitted. The cooperative contribution,

$$\Delta U(n, \text{coop}) \equiv U(n) - U(n, \text{non-coop}), \quad (8)$$

is  $-2.005 \times 10^{-3}$  a.u. for the tetramer of Table 2. The relative contribution increases regularly:

$$\Delta U(n, \text{coop})/U(n) = \{\text{dimer: } 0.0169 \text{ Trimer: } 0.0291; \text{tetramer: } 0.0522; \quad (9)$$

ices (Ih, II, IX): (0.15 to 0.19, 0.20, 0.18)}. Let the dimer energy for each  $\langle \alpha, \beta \rangle$  in the non-additivity definition be  $U(2, \langle \alpha, \beta \rangle)$ . Then the nonadditive contribution,

$$U(n, \text{NA}) = U(n) - \sum_{\{\langle \alpha, \beta \rangle\}} U(2, \langle \alpha, \beta \rangle), \quad (10)$$

contains a cooperative contribution. The calculated value [1] for the optimal trimer of [2],  $U(3, \text{NA}) = -1.783 \times 10^{-3}$ , compares with the tetramer value,  $U(4, \text{NA}) = -5.361 \times 10^{-3}$  a.u. The relative contributions are:

$$|U(n, \text{NA})/U(n)| = \{\text{trimer, } 0.083; \text{tetramer, } 0.1396\}. \quad (11)$$

Comparison of Eq. (11) with Eq. (9) suggests, as is to be expected, that the relative non-additive contribution for the ices is even larger than the cooperative contribution,  $\sim 0.15$  to  $0.20$ .

A third quantity, the non-additive contribution calculated in a non-cooperative approximation,

$$U(n, \text{NA, non-coop}) = U(n) - \sum_{\{\langle \alpha, \beta \rangle\}} U(2, \langle \alpha, \beta \rangle, \text{non-coop}), \quad (12)$$

has been used recently [8]. Therefore, we have calculated this quantity as well. For the optimal trimer (tetramer), the differences are  $U(n, \text{NA}) - U(n, \text{NA, non-coop}) = 3.701 \times 10^{-3}$  ( $1.462 \times 10^{-2}$ ) a.u. This yields the relative errors,

$$\{U(n, \text{NA}) - U(n, \text{NA, non-coop})\}/U(n, \text{NA}) = 0.207(0.273). \quad (13)$$

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