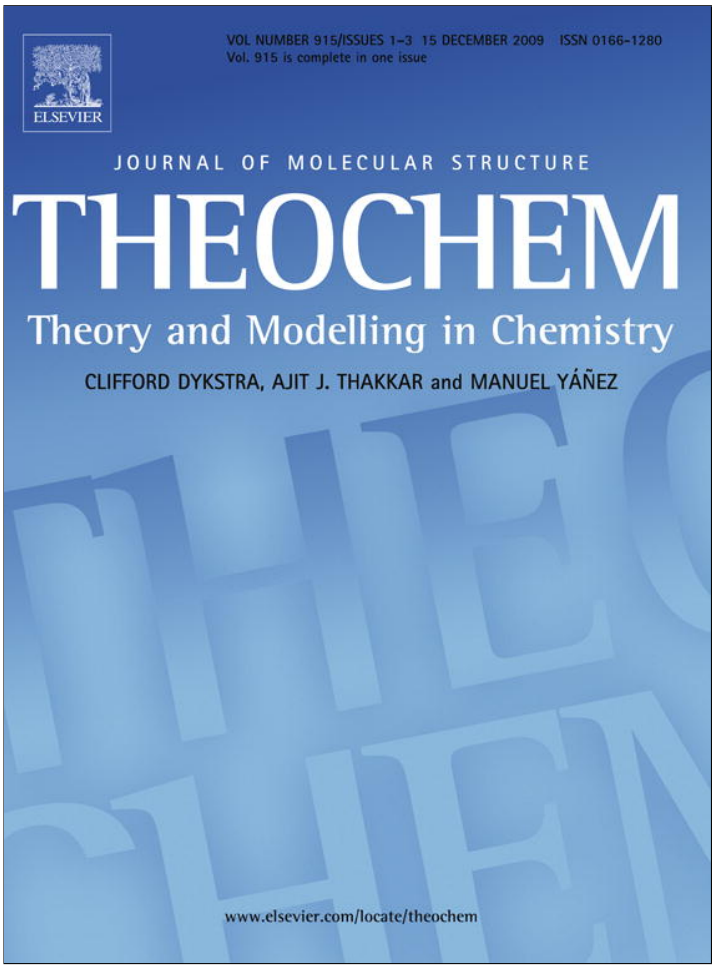

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# Electrical field effects on dipole moment, structure and energetic of $(H_2O)_n$ $(2 \leqslant n \leqslant 15)$ cluster

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ABSTRACT

The effect of an external electric field on water clusters of the $(H_2O)_n$ type, with $[1 \leqslant n \leqslant 15]$, in the ground state was analyzed at the B3LYP/cc-pVTZ level of theory. The calculations showed that an external electric field changes the number of hydrogen bonds, reduces the cluster sizes and increases the strength of the inter-cluster hydrogen bonds. The particular symmetry of the cluster and the null dipole moment in these specific configurations suggest that their stability can be associated with a perfect alignment of the water molecules, maximizing attractive electrostatic interactions caused by changes in the charge distribution of the clusters.



## 1. Introduction

Water is essential to all known forms of life. It is a key component in determining the quality of our lives. There is a surprising connection between the quality of water and healthful longevity [1]. It is necessary for the digestion and absorption of food, helps to maintain proper muscle tone, supplies oxygen and nutrients to the cell, etc. [2,3]. Its anomalous properties are responsible for many studies in the literature [4–17] although several possibilities remain to be explored.

In order to understand some of the water properties, it is necessary to know its geometry and electronic structure under different circumstances. Theoretical methods represent an important way to provide a physical understanding or to accurately predict specific behaviors where experimental information would be difficult or even impossible. A simple search in the literature will indicate a large set of calculations providing useful information about single water molecules or clusters or even simulations involving hundreds of water monomers in order to provide acceptable information to explain experimental observations or tendencies. For instance, theoretical studies of some properties of water over a range of temperatures between 5 and 65 °C, investigated by Lin and Brown [18] using principal component regression (PCR) and multiline regression (MLR) models, were in excellent correlation with near-IR spectroscopy showing the susceptibility of the liquid structure with the temperature and pressure changes. These two intensive variables can modify the clustering of water molecules and the respective sizes favor water property changes [18], as intuitively expected, resulting in the formation of larger clusters for lower temperatures.

Harvey et al. [19] predicted the ultraviolet (UV) spectrum of water clusters using a semi-empirical model developed to provide representations of excited-state potential-energy surfaces for $(H_2O)_n$, $n = 2$–6. Each arrangement has its maximum light absorption at a specific frequency, suggesting that water clusters of different sizes present different electronic characteristics.

Theoretical calculations and tunneling spectrometry investigations of $(H_2O)_n$ ($n = 2$–6) cluster sizes, number of hydrogen bonds and lower energy structures, by researchers from Berkeley–California, showed that these parameters were closely related to some water properties such as viscosity and surface tension [20–25]. In 2001, high resolution spectra of the vibrational movements of water trimmers were obtained for the first time for $(H_2O)_3$ and $(D_2O)_3$ [24,25], revitalizing even more the cluster model for the water structure. In 1992 the structures, binding energies and cooperative effects in the water trimer were studied at high levels of theory [17].

In the gas phase, Lee et al. used density functional theory to study the conformations and the binding energies of water clusters formed by up to 20 molecules. The determination of the most stable structures became considerably more difficult above six water molecules and the number of conformations increased drastically with the number of water molecules. Curiously, the most stable clusters, built by multiples of four water molecules (4, 8,

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12, etc.), presented an extra stability compared to the other conformations [5]. The authors established a correlation between the binding energy of the water clusters with the respective sizes, estimating the binding energy ($-11.38$ kcal mol$^{-1}$) in excellent agreement with the experimental value of the sublimation energy of ice ($-11.35$ kcal mol$^{-1}$).

Some papers agree that the liquid water structure is a mixture of clusters of various sizes and forms [20–23]. This cluster model was suggested in 1957 when Frank and Wen [26] described liquid water as having ice-like structures, to a greater or lesser degree, determined by the hydrogen bonds that depend on the temperature and pressure of the system.

The numbers associated with the most stable clusters have been referred to as magic numbers [5]. The sequence of magic numbers carries essential information about the electronic and ionic structure of the cluster and consequently the water properties. Considering the intrinsic relation between the water properties and the most stable clusters, a modification of the magic numbers or, explicitly, the most stable structures may provide new physical–chemical insights and possibly alternative perspectives of the structural effect on the electronic properties of water.

A simple way to induce changes in the stability of the clusters would be through perturbation by a magnetic or electric field. Some experimental evidence indicates that water in magnetic fields presents different properties compared to untreated water [27]. Some authors attribute these alterations to the weakening or breaking of hydrogen bonds changing the water structure to a new one or to a new combination of clusters [28,29]. Changes in solution enthalpy [30], water adsorption on surfaces [31], crystallization and salt precipitations [32,33], irrigation of plants [34–37], and hydrodynamic effects [38,39] are observed when the water is submitted to the action of magnetic fields. The many possibilities for electric field applications have been stimulated by researchers [40].

In 1962 Zawidzki [41] observed "ice-whiskers" formation in a cloud and in an electric field. Others authors, after applying an electric field in water saw a change in the nucleation temperature of the ice [42–44]. The electric field can be used to induce the phase transition of water-in-oil emulsions [45–50] and to deform water droplets [51,52], to change the adsorption velocity [53,54].

The electric field created by charges [55,56] or external electric field has been used to study the hydrogen bond [57,58].

The electric field, temperature, pressure or density can cause fluctuations in the strength or distance of the hydrogen bond [59]. The weakening or strengthening of the hydrogen bond can be explained in terms of a high polarizability of the molecular orbital with respect to the direction of the electric field applied [60].

Batista et al. have found alternatives to reduce the computational cost and to understand the behavior of water under an electric field effect [61]. Svishchev and Kusalik [62] applied a homogeneous electric field to equilibrated liquid water in the process of molecular dynamics simulation. They observed the possibility of obtaining solidified water or ice Jung [63] discovered that more organized structures can be made in liquid water under very a strong electric field. Choi [64] observed that the H bond to cluster ($n = 3$–5) is weakened. However, research [60,65] shows that the results depend on the force and direction of the applied electric field. Thus, the application of an electric field on water molecules may have several possibilities to be explored. For instance, in biological systems, the hydrogen bonding network plays a dominant role in determining the intra-molecular proton transfer [58].

The present work is a preliminary computational experiment devoted to explore and analyze the theoretical consequences of the presence of an electric field on the electronic properties of water clusters of the $(H_2O)_n$ type, with $[1 \leqslant n \leqslant 15]$, in the ground state using density functional theory.

## 2. Computational methods

The calculations were performed at the density functional theory (DFT), which has been shown to be a promising alternative to describe the structures and the energies of different kinds of hydrogen-bonded clusters [40,66–70] with Becke's three-parameter exchange functional and the Lee, Yang, and Parr (B3LYP) gradient-corrected functional [71,72], which has been shown to provide important information about structures and energetic of different hydrogen bond networks in water [40,67,69] and to predict the ground-state electrical structures, reaction energetic and molecular geometry [70]. This combined functional has been used in the literature and is pointed out as particularly accurate in the calculation of molecular magnetic and electric properties [73,74] and in a successful application in the study of hydrogen-bonded clusters using DFT [75–77]. The cc-pVTZ (polarized triple-zeta) basis set was used for all calculated properties because it produces the fewest errors [78].

Considering that electric fields can change the geometries and electronic properties and in view of the large number of possible geometries for the larger clusters, yielding several minima on a shallow potential-energy surface and making the location of the true energy minimum for each cluster extremely difficult, in this work the water cluster coordinates were kept frozen and were taken from the literature [75,79]. Therefore this paper will focus attention only on the electronic changes.

The influence of the external electric field on the ground state electronic properties was studied using single-point energy calculations along with water cluster geometries obtained from the literature [75,79]. The electric field (EF) is defined as uniform and aligned along the $X$ direction [71,80,81], which is comparable with most experimental measurements [82]. The influence of the EF intensity and direction on water clusters was investigated in an earlier work [82].

In this paper, all the calculations were carried out using Gaussian 03 program [83]. The topological properties of HBs in the water clusters were characterized using the AIM theory of Bader [84–88].

## 3. Results and discussion

### 3.1. Intra- and inter-cluster binding energies

The molecular interaction energy was calculated using the following equation:

$$\Delta E_b = [E(\text{cluster}) - nE(\text{monomer})]/n \quad (1)$$

where $\Delta E_b$ is the intra-cluster binding energy for the water molecule of the cluster, $n$ is the number of water molecules of the cluster and $E$(monomer) is the energy of the monomer under the same conditions as the clusters.

Since more than two monomers are being considered, the BSSE method was defined as [80,81,89] (see below equation):

$$\Delta E' = \left[E(\text{cluster}) - \left\{E\left(H_2O^{(1)}\right) + E\left(H_2O^{(2)}\right) + \cdots + E\left(H_2O^{(n)}\right)\right\}\right]/n \quad (2)$$

where $\Delta E'$ is the binding energy per water molecule taking into account the BSSE correction; $E(H_2O^{(1)})$, $E(H_2O^{(2)})\cdots E(H_2O^{(n)})$ are

**Table 1**
Vaporization enthalpy and surface tension.

| | $\Delta H_{vap}$ (kJ mol$^{-1}$) | $\gamma$ (N m$^{-1}$ × 10$^{-3}$) |
|---|---|---|
| Water [82] | 50.86 ± 0.46 | 72.27 ± 0.37 |
| Magnetized water [82] | 68.86 ± 0.49 | 75.50 ± 0.23 |
| Theoretical [106] | 44.12 | 72.27 |

**Table 2**
*A* and *B* coefficients (Eq. (3)) to calculate the binding energy of a bulk system in the presence of an external electric field.

| Field (a.u.) | *B* (kcal mol$^{-1}$) | *A* (kcal mol$^{-1}$) |
|---|---|---|
| 0.00 | −12.2931 | 18.5934 |
| $2.0 \times 10^{-4}$ | −12.3245 | 18.7189 |
| $4.0 \times 10^{-4}$ | −12.3308 | 18.8005 |
| $6.0 \times 10^{-4}$ | −12.3433 | 18.8883 |
| $8.0 \times 10^{-4}$ | −12.3496 | 18.9762 |
| $3.9 \times 10^{-3}$ | −12.4970 | 20.3380 |
| $6.8 \times 10^{-3}$ | −12.6110 | 21.6110 |
| $1.0 \times 10^{-2}$ | −12.7889 | 23.0174 |
| $2.0 \times 10^{-2}$ | −13.1082 | 26.8857 |

the total energies of individual water molecules in the presence of all the ghost molecules present in the cluster. These total energies are calculated individually for each molecule forming the cluster.

The binding energy of the bulk system (intra and inter) was calculated using Eq. (3), as suggested by Lee et al. [5]:

$$\Delta E = A/n + B \tag{3}$$

The water interaction energy when $n \to \infty$ was compared with the sublimation enthalpy of water at 0 K from the literature, excluding the zero point energy and corresponds to −11.3 kcal mol$^{-1}$ [90]. Table 2 shows the *A* and *B* parameters determined for the clusters studied in this work. The results for $\Delta E_b$ and $\Delta E$ for $n \to \infty$ are in Tables 3 and 4, respectively. The *B* constant in Eq. (3) corresponds to the binding energy of the bulk system (intra and inter).

In order to evaluate our theoretical strategy, we performed dipole calculations at the MP2/6-311++G(2d,2p) level of theory in the absence of an electric field and we observed that MP2 results

**Table 3**
Intra-cluster binding energies for $n \to \infty$ calculated at the B3LYP/cc-pVTZ level of theory at the equilibrium geometry.

| Field (a.u.) | $\Delta E$ (kcal mol$^{-1}$) |
|---|---|
| Experimental [2] | −11.300 |
| 0.00 | −12.293 |
| $2.0 \times 10^{-4}$ | −12.324 |
| $4.0 \times 10^{-4}$ | −12.330 |
| $6.0 \times 10^{-4}$ | −12.343 |
| $8.0 \times 10^{-4}$ | −12.349 |
| $3.9 \times 10^{-3}$ | −12.497 |
| $6.8 \times 10^{-3}$ | −12.611 |
| $1.0 \times 10^{-2}$ | −12.788 |
| $2.0 \times 10^{-2}$ | −13.108 |

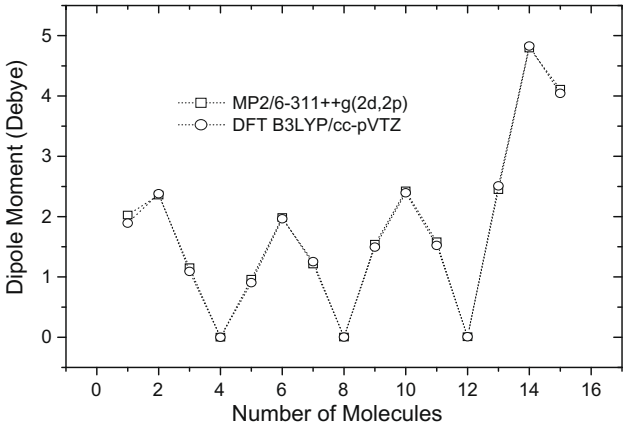


**Fig 1.** Dipole moments for water clusters with no applied external electric field at MP2/6-311++G(2d,2p) and B3LYP/cc-pVTZ levels.

are in a good agreement with DFT data (Fig. 1). In addition, the results show that the binding energies calculated by the DFT method reproduce the experimental data (Table 2) and also theoretical results predicted by highly correlated calculation, which are computationally more expensive *ab initio* methods. It is important to mention that the structural values and frequencies obtained from DFT may correspond, on similar systems, to those predicted by pos-HF methods, such as MP2 method [40,91]. In this way, aiming at reducing the computational demand, the calculations were carried out at DFT level with cc-pVTZ.

It is observed that, in the absence of an electric field, the binding energy shows only a small deviation from the experimental result, demonstrating the reliability of the theoretical methodology. Calculations performed using the methods described above show that clusters of higher symmetry often possess relatively low energy [92]. Thus, the symmetric cluster configurations are often of particular interest. The process of searching the symmetric cluster configurations can be speeded up significantly. Then, to make sure that our calculations are correct, we selected the cluster geometries from previous papers [75] (see Fig. 2). Herein, we are interested in the investigation of the hydrogen bond network rearrangement dynamics due just to electric field effects, which promise to enhance our understanding of solid and liquid water behavior. It should be kept in mind that low energy structures are likely to have higher effective symmetry [92]. Studies developed by Nelson and co-workers with a model polypeptide reinforce the importance of the symmetry in biological systems [93]. Thus, in this paper, we addressed this issue.

**Table 4**
Intra-cluster energies (kcal mol$^{-1}$) of water molecules in the presence of an external electric field (a.u.) of different intensities.

| | 0.0000 | 0.0002 | 0.0004 | 0.0006 | 0.00068 | 0.0039 | 0.0068 | 0.0100 | 0.0200 |
|---|---|---|---|---|---|---|---|---|---|
| $(H_2O)_2$ | −2.89552 | −2.86028 | −2.80175 | −2.74322 | −2.6847 | −1.7806 | −0.9338 | −0.0036 | 2.8868 |
| $(H_2O)_3$ | −6.17103 | −6.17395 | −6.17338 | −6.17283 | −6.17228 | −6.1662939 | −6.1582 | −6.1531 | −6.15261 |
| $(H_2O)_4$ | −7.98339 | −7.98797 | −7.98814 | −7.98833 | −7.98853 | −7.9944856 | −7.9982 | −8.0064 | −8.04756 |
| $(H_2O)_5$ | −8.29284 | −8.30064 | −8.30243 | −8.30423 | −8.30604 | −8.3344596 | −8.3652 | −8.4007 | −8.53078 |
| $(H_2O)_6$ | −8.85282 | −8.87201 | −8.88385 | −8.89571 | −8.90759 | −9.0954736 | −9.2709 | −9.4704 | −10.1237 |
| $(H_2O)_7$ | −9.47237 | −9.47760 | −9.47116 | −9.46473 | −9.45831 | −9.361286 | −9.2679 | −9.1682 | −8.86513 |
| $(H_2O)_8$ | −10.4687 | −10.4709 | −10.4710 | −10.4712 | −10.4714 | −10.473611 | −10.474 | −10.477 | −10.4806 |
| $(H_2O)_9$ | −10.4375 | −10.4458 | −10.4479 | −10.4500 | −10.4521 | −10.487602 | −10.519 | −10.557 | −10.6904 |
| $(H_2O)_{10}$ | −10.6855 | −10.6964 | −10.6987 | −10.7010 | −10.7033 | −10.741077 | −10.773 | −10.811 | −10.9331 |
| $(H_2O)_{11}$ | −10.3896 | −10.3859 | −10.3799 | −10.3738 | −10.3678 | −10.278343 | −10.195 | −10.109 | −9.34098 |
| $(H_2O)_{12}$ | −11.1233 | −11.1383 | −11.1384 | −11.1386 | −11.1389 | −11.1462 | −11.153 | −11.167 | −10.3994 |
| $(H_2O)_{13}$ | −10.6362 | −10.7910 | −10.8002 | −10.8094 | −10.8186 | −10.966006 | −11.105 | −11.2647 | −11.8039 |
| $(H_2O)_{14}$ | −10.2226 | −10.2079 | −10.1912 | −10.1746 | −10.1579 | −9.90249 | −9.6619 | −9.40076 | −8.60326 |
| $(H_2O)_{15}$ | −11.3319 | −11.3209 | −11.3078 | −11.2948 | −11.2817 | −11.083144 | −10.897 | −10.6974 | −10.1033 |

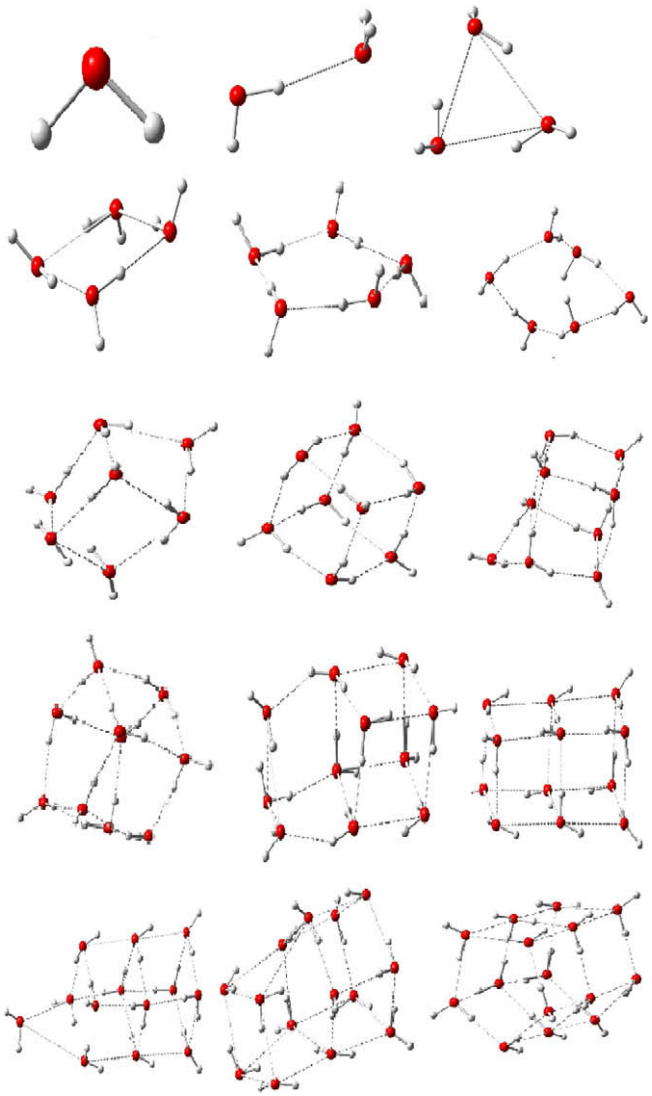

**Fig. 2.** Equilibrium structures of different clusters water.

Table 3 also shows that the increase in magnitude of the field decreases the intra-cluster binding energy; these results agree well with other results from the literature [29].

When the electric field is applied, an alteration in the intra-cluster binding energy of the water clusters is observed. Thus, for the smaller external electric fields a visible variation of cluster stability was not observed. However, for higher electric field magnitudes a significant alteration of the intra-cluster binding energy is observed. It should be kept in mind, however, that all water molecule clusters were sensitive to the electric field employed.

Nowadays, more information has been extracted by observing alterations of physical properties of water. In addition, some experimental evidences indicate that water in magnetic fields can present similar properties compared to water in electric fields [27]. Water treatment by magnetic or electric fields is still a controversial subject, because the available results have low reproducibility and little consistency, which reinforce the need for studies using theoretical and experimental techniques.

Recent studies have found that the electric field influences the physical–chemical properties [94,95] such as surface tension and vaporization enthalpy. It is well-known that surface tension ($\gamma$) and vaporization enthalpy ($\Delta H_{vap}$) are properties that are correlated with the intermolecular forces [96]. So, changes in these properties can be related with changes in these forces. The values for enthalpy and surface tension are reported in Table 1. All measurements were carried out at the same temperature (295 K) and treatment conditions with the intention to reduce errors. It is important to mention that the results were submitted to variance analysis and *T*-test for validation of the increase tendencies of the measured parameters.

The results reveal that the surface tension and vaporization enthalpy increased when the water was submitted to the electric/magnetic treatment [97,98]. An increase in these physical–chemical properties means an increase in the molecular interactions. However, in light of our rationalization, those hydrogen bonds (HBs) can be inter- and intra-cluster. If clusters are only present in the gaseous phase, during the vaporization process many of the inter- and intra-interactions are broken.

On the other hand, the inter cluster interactions are more important to the surface tension than the intra. Thus, an increase of these properties can be related to the increase of the inter clusters interactions.

Whereas the electric field decreases the intra-cluster binding energy ($\Delta E_b$) for the water molecule of the cluster (Fig. 3), it is observed that the values of surface tension and vaporization enthalpy increased with the electric field. In fact, that evidence reinforces the importance of the intermolecular interactions.

Therefore, we may suggest that the electric field weakens the intra-cluster hydrogen bonds, breaking the larger clusters, forming smaller clusters with stronger inter-cluster hydrogen bonds, which is especially noted for clusters with $n = 4, 8, 12, \ldots$. The competition between the inter- and intra-cluster interactions in the $Fe_4(PO_4)_3(OH)_3$ system has been reported in the literature [99]. However, discussions of these two interactions for water have not been found to date.

### 3.2. Alterations of physical properties of water

It is clear from Fig. 3 that the electric field decreases the stability of each cluster. This means that the external field can cause a weakening of intra-cluster H bonds and reduce the average number of hydrogen bonds between water molecules. This shows that the content of monomer water molecules and dimer water molecules will increase if water is exposed to an electric field. In other words, larger clusters are broken to form smaller ones.

Thus, our observations are just focused on the strength of the hydrogen bonds. In line with this observation, a conclusion can be made that an external electric field can weaken hydrogen bonds

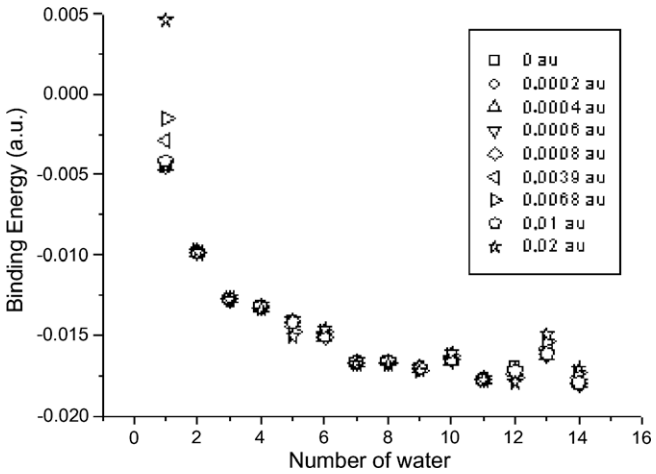


**Fig. 3.** Energy variations in the presence of an external electric field of different intensities.

or reduce the mean number of hydrogen bonds. Zhou [29], using theoretical calculations, suggested that the application of a magnetic field favored the breaking of the cluster connections, obtaining smaller clusters with a higher number of neighbors, showing how the effect of a magnetic field is similar to the electric field.

The binding energy in Fig. 3 and Table 4 show that the clusters with 4, 8 and 12 water molecules are relatively stable compared to other water clusters. The stable conformer of the water cluster tends to form a maximum number of planar three–four member rings, as already noted by Lee et al. [5,99], who correlated various properties of water clusters, from 2 to 10 monomers, to their respective sizes and verified that the dipole moments are zero for the clusters involving 4 and 8 monomers. The symmetry properties of the water clusters containing these magic numbers are always zero indicating a perfect arrangement between the dipoles, which can be pointed out as being responsible for the greater stability of these clusters. Hydrogen bonds are usually considered to be strongly dependent on electrostatic interactions. Considering this hypothesis, the larger stability of water clusters containing magic numbers can be related to the predominance of electrostatic effects over van der Waals or other intermolecular effects. The lower stability for those clusters containing magic numbers + 1 also reflects the difficulty of stabilization of the electrostatic interaction because the previous systems distributed the electronic charge on an uniform way resulting in a null dipole moment.

Fig. 4 shows that the magic numbers have a dipole moment equal to zero, so the relative stability of the magic number ($n = 4, 8, 12, \ldots$) can be explained, at the molecular level, as due to an arrangement between the dipoles, which can be indicated as responsible for the stability of water clusters. In addition, Fig. 5 shows that an increase of the electric field decreases the stability of the magic number, but increases the stability of other clusters.

In an earlier work [82], we observed that magnetic field increase weakened the intra-cluster bonds, therefore smaller clusters were formed. Now, we can see that the electric field decreases the stability of the magic numbers. In other words, the intra-cluster bonds are being weakened and smaller clusters are being formed. The cluster of magic number 4 is weakened, so the number 2 cluster has its stability increased, number 8 is also weakened and number 7 becomes stronger, finally number 12 is also weakened, but number 11 has an increased stability. Number 16 is known as a magic number (planar ring) and we see in Fig. 4 that the number 15 has become stronger. Therefore, our results suggest that the electric field weakened the magic numbers, forming stronger smaller clusters, because the electric field significantly changes the charge distribution in the water clusters.

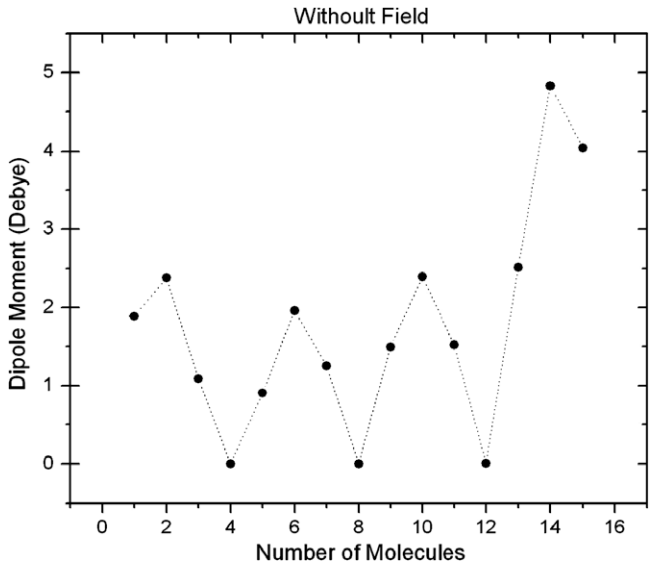


**Fig. 4.** Dipole moments for water clusters with no applied external electric field.

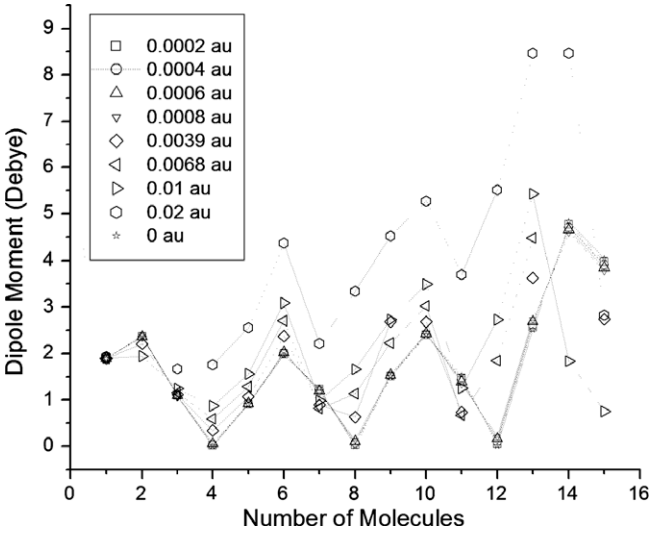


**Fig. 5.** Dipole moments for water clusters in the presence of an external electric field.

### 3.3. HB intensity of $(H_2O)_n$ clusters

Theoretically, some methods are commonly used to estimate the intra- or intermolecular HBs. One of them is the energy assessment, where the HB intensity can be measured by the energy differences between polymer and monomers (see Eq. (2)). The other is the electron density assessment, where the HB intensity can be used to measure the spatial electron density of the region between two associated atoms. The former is very efficient if the precise energy is obtainable. However, for large-size molecules or complexes, such as those in this work, it is difficult to obtain the precise energy of a complex. Therefore we used the electron density assessment instead. The electron distribution of a molecule is an excellent starting point to gain chemical insight into a molecule or an aggregate of molecules [100]. Among all known electron density methods, an appealing theory that takes advantage of this observation is the "Atoms in Molecules" model (AIM) [60], which is based on the charge density partition of a molecule into atoms in a natural way by using the concept of gradient path. Integration of properties over these atomic basins is one of the cornerstones of AIM [101,102]. For example, hydrogen bonding (both ordinary and exotic) can be confirmed solely from the charge density based on a handful of criteria, some of which invoke integrated atomic properties [103]. This is the reason why we have chosen the AIM theory to study the intra-molecular HBs of the complexes in this work.

In line with that, the bonding characteristics of the clusters studied have been investigated through the use of the atoms in molecules (AIM theory of Bader) [60,104]. For this purpose, we have located the bond critical points, i.e., points where the charge density function ($\rho(r)$) is a minimum along the bond path and maximum in the other two directions, because, as it has been shown in the literature [103,105,106] that a fairly good linear correlation exist between the charge densities at the HB bond critical points and the strength of the linkages. We have also evaluated the Laplacian of the charge density ($\nabla^2\rho(r)$).

As mentioned before, the AIM approach provides a rigorous procedure based upon the topology of density $\rho(r)$ to partition the molecule into atomic fragments × bound by a zero flux surface for the gradient vector field of $\rho(r)$. A crucial element of the theory is the set of properties of the critical points in $\rho(r)$, the points lying between bonded atoms are called bond critical points (BCPs). The BCP is a minimum of $\rho(r)$ along the bond path and a maximum in the interatomic surface. Local properties at BCPs convey valuable information about the molecular structure. The former is typically associated with interactions between closed-shell systems (ionic bonds, hydrogen bonds, and van der Waals forces), whereas the latter characterizes covalent bonds, where the electron density concentrates in the internuclear region. Our study on the electronic topologies of the $(H_2O)_n$ $(2 \leqslant n \leqslant 15)$ cluster was concentrated on the BCPs with positive $\nabla^2\rho(r)$ ($\nabla^2\rho(r) > 0$). The existence of HB can be estimated by a BCP with a positive $\nabla^2\rho(r)$ (i.e. $\nabla^2\rho(r) > 0$) and an order of magnitude hundredth (i.e. $10^{-2}$) of $\rho(r)$ value [103].

The AIM analysis of its electron density distribution, $\rho(r)$, was carried out to investigate the HBs inside the clusters and revealed a bond critical point (BCP) in all the internuclear region O···H.

The results reported in Table 5 and Fig. 6 suggest that the electric field can indeed generate a weakening of intra-cluster H bonds decreasing an consequently the stability of each cluster. It is noteworthy that the highest $\rho(r)$ value (0.02939), indicating that this HB was the strongest among the four HBs. For instance, for the cluster with 15 and 14 molecules the strongest electric field (0.02 a.u.) is associated with the lowest $\rho(r)$ value (0.02122), and the highest $\rho(r)$ value is correlated to weakest electric field (Table 5).

It is also well-known that both have low $\rho(r)$ values and long the bond path length (BPL), imply a weak intermolecular HB. BPL is regarded as the approximate distance (usually slightly overestimated) of H—Y out of the X–H—Y formation.

It should be kept in mind, however, that the distance among atoms is kept fixed for each cluster, thus, the strength of the hydrogen bond is determined predominantly by the electric field effects. Hence, the related effect to the BPL is constant and can be neglected along the different electric fields employed. In this way, by taking the values at the equilibrium position as a function of the applied field, it is possible to study the continuous variation of the BCP properties while keeping in all cases the system at its equilibrium configuration.

Interestingly, the $\rho(r)$ values put in evidence that the clusters with 4, 8 and 12 water molecules have hydrogen bonds usually considered to be relatively stronger when we compare to other water clusters. That information reinforces our previous findings using the binding energy per water molecule ($\Delta E$), which suggest that clusters of higher symmetry often present higher stability, which is in good agreement with previous findings. In this line, the results point out that the stability of the water clusters can be related with a perfect alignment of the water molecules, maximizing attractive electrostatic interactions.

## 4. Conclusion

In this work, the effect of an electric field on water clusters has been examined. It was shown that an external electric field influences the number of hydrogen bonds, the water structure, and the self-diffusion coefficient of the water molecules. The results suggest that the hydrogen bonds are broken, which increases the force of the remaining bonds. From our theoretical data, we may conclude that the competition between different hydrogen bond networks (intra- and inter-molecular) gives rise to the weakening of the intra-cluster hydrogen bonds, forming smaller clusters with stronger inter-cluster hydrogen bonds.

**Table 5**
Electron density ($\rho$) and Laplacian ($\nabla^2\rho$) of the bond critical points for intermolecular hydrogen bonds in the water clusters studied.

| | 0.0000 | | 0.0002 | | 0.0004 | | 0.0006 | | 0.00068 | | 0.0039 | | 0.0068 | | 0.0100 | | 0.0200 | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $\rho$ | $\nabla^2\rho$ | $\rho$ | $\nabla^2\rho$ | $\rho$ | $\nabla^2\rho$ | $\rho$ | $\nabla^2\rho$ | $\rho$ | $\nabla^2\rho$ | $\rho$ | $\nabla^2\rho$ | $\rho$ | $\nabla^2\rho$ | $\rho$ | $\nabla^2\rho$ | $\rho$ | $\nabla^2\rho$ |
| 2 | 0.02105 | 0.07015 | 0.02073 | 0.06911 | 0.02075 | 0.06918 | 0.02079 | 0.06931 | 0.02072 | 0.06905 | 0.02126 | 0.07088 | 0.02153 | 0.07176 | 0.02226 | 0.0742 | 0.02257 | 0.07523 |
| 3 | 0.02435 | 0.08215 | 0.02397 | 0.07991 | 0.02398 | 0.07993 | 0.02406 | 0.08021 | 0.02390 | 0.07968 | 0.02515 | 0.08382 | 0.02575 | 0.08584 | 0.02451 | 0.08166 | 0.02443 | 0.08143 |
| 4 | 0.02842 | 0.09134 | 0.02554 | 0.08513 | 0.02552 | 0.08506 | 0.02556 | 0.08520 | 0.02549 | 0.08498 | 0.02631 | 0.08770 | 0.02628 | 0.08760 | 0.02685 | 0.08951 | 0.02587 | 0.08622 |
| 5 | 0.02608 | 0.08693 | 0.02617 | 0.08724 | 0.02613 | 0.08709 | 0.02612 | 0.08705 | 0.02617 | 0.08724 | 0.02575 | 0.08583 | 0.02558 | 0.08527 | 0.02462 | 0.08205 | 0.02437 | 0.08123 |
| 6 | 0.02421 | 0.08732 | 0.02642 | 0.08806 | 0.02636 | 0.08787 | 0.02633 | 0.08776 | 0.02644 | 0.08815 | 0.02561 | 0.08532 | 0.02524 | 0.08412 | 0.02373 | 0.07911 | 0.02614 | 0.08713 |
| 7 | 0.02690 | 0.08897 | 0.02663 | 0.08878 | 0.02657 | 0.08856 | 0.02656 | 0.08852 | 0.02665 | 0.08883 | 0.02612 | 0.08706 | 0.02592 | 0.08641 | 0.02432 | 0.08107 | 0.02463 | 0.0821 |
| 8 | 0.02846 | 0.09486 | 0.02736 | 0.09119 | 0.02727 | 0.09091 | 0.02734 | 0.09115 | 0.02732 | 0.09105 | 0.02815 | 0.09384 | 0.02862 | 0.09541 | 0.02819 | 0.09397 | 0.02732 | 0.09105 |
| 9 | 0.02759 | 0.09196 | 0.02696 | 0.08987 | 0.02689 | 0.08964 | 0.02693 | 0.08977 | 0.02694 | 0.08982 | 0.02722 | 0.09074 | 0.02742 | 0.09141 | 0.02666 | 0.08886 | 0.0239 | 0.07965 |
| 10 | 0.02752 | 0.09176 | 0.02754 | 0.09193 | 0.02744 | 0.09148 | 0.02746 | 0.09153 | 0.02757 | 0.09191 | 0.02748 | 0.09161 | 0.02751 | 0.09171 | 0.02503 | 0.08342 | 0.02617 | 0.08723 |
| 11 | 0.02753 | 0.09174 | 0.02661 | 0.08881 | 0.02654 | 0.08845 | 0.02656 | 0.08852 | 0.02661 | 0.08870 | 0.02659 | 0.08863 | 0.02658 | 0.08860 | 0.02413 | 0.08043 | 0.02689 | 0.08965 |
| 12 | 0.02939 | 0.09772 | 0.02843 | 0.09492 | 0.02833 | 0.09444 | 0.02836 | 0.09453 | 0.02835 | 0.09453 | 0.02839 | 0.09462 | 0.02826 | 0.09423 | 0.02594 | 0.08646 | 0.02561 | 0.08538 |
| 13 | 0.02665 | 0.08877 | 0.02571 | 0.08561 | 0.02564 | 0.08546 | 0.02567 | 0.08555 | 0.02577 | 0.08591 | 0.02570 | 0.08566 | 0.02571 | 0.08572 | 0.02322 | 0.07741 | 0.02327 | 0.07756 |
| 14 | 0.02572 | 0.08575 | 0.02489 | 0.08270 | 0.02474 | 0.08248 | 0.02476 | 0.08252 | 0.02484 | 0.08282 | 0.02479 | 0.08263 | 0.02478 | 0.08264 | 0.02234 | 0.07445 | 0.02164 | 0.07214 |
| 15 | 0.02483 | 0.08278 | 0.02397 | 0.07983 | 0.02385 | 0.07949 | 0.02386 | 0.07953 | 0.02388 | 0.07961 | 0.02389 | 0.07963 | 0.02385 | 0.07951 | 0.02143 | 0.07142 | 0.02122 | 0.07072 |

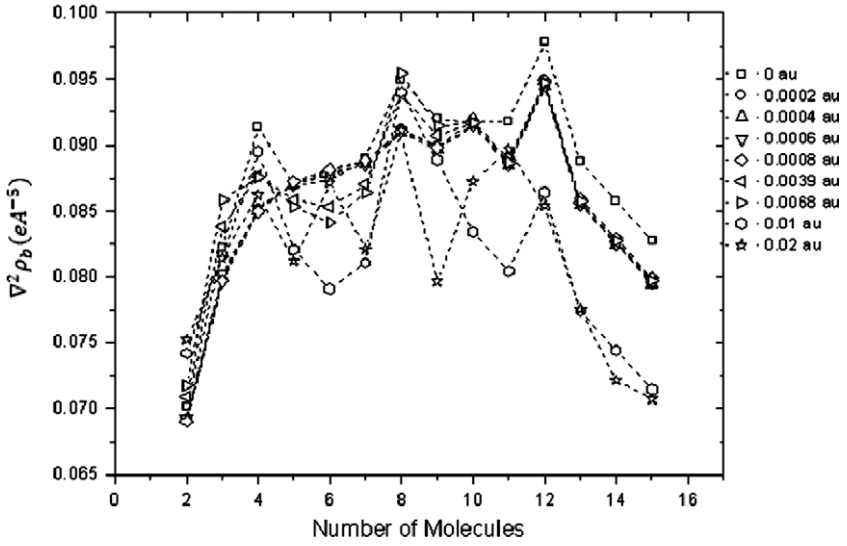


**Fig. 6.** Variations of Laplacian ($\nabla^2\rho$) in the presence of an external electric field of different intensities for water clusters.

It is worth noting that the particular cluster with the null dipole moment suggests that stability can be associated with a perfect alignment of the water molecules, maximizing attractive electrostatic interactions. When the electric field is applied, it changes the charge distribution in the clusters, the magic numbers are weakened and smaller clusters become stronger.

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