

Many-body energies during proton transfer in an aqueous system

Ajay Chaudhari · Gul Afroz Meraj · Shyi-Long Lee

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Abstract The energetics of the mechanism of proton transfer from a hydronium ion to one of the water molecules in its first solvation shell are studied using density functional theory and the Møller–Plesset perturbation (MP2) method. The potential energy surface of the proton transfer mechanism is obtained at the B3LYP and MP2 levels with the 6-311++G** basis set. Many-body analysis is applied to the proton transfer mechanism to obtain the change in relaxation energy, two-body, three-body and four-body energies when proton transfer occurs from the hydronium ion to one of the water molecules in its first solvation shell. It is observed that the binding energy (BE) of the complex decreases during the proton transfer process at both levels of theory. During the proton transfer process, the % contribution of the total two-body energy to the binding energy of the complex increases from 62.9 to 68.09% (39.9 to 45.95%), and that of the total three-body increases from 25.9 to 27.09% (24.16 to 26.17%) at the B3LYP/6-311++G** (MP2/ 6-311++G**) level. There is almost no change in the water–water–water three-body interaction energy during the proton transfer process at both levels of theory. The contribution of the relaxation energy and the total four-body energy to the binding energy of the complex is greater at the MP2 level than at the B3LYP level. Significant differences are found between the

relaxation energies, the hydronium–water interaction energies and the four-body interaction energies at the B3LYP and MP2 levels.

Keywords Hydronium ion · Many-body analysis · Proton transfer mechanism

Introduction

Proton transfer is one of the important processes in chemistry and biology. The hydrogen bonded network of water plays an important role in such transfers. Proton transport properties are of great interest for various applications, such as fuel cells, water electrolysis, chloro-alkali technologies, electro-organic synthesis, catalysis, separations, sensors, and electrode coatings. In bulk water, each water molecule forms four hydrogen bonds. It acts as a hydrogen bond donor for two hydrogen bonds and a hydrogen bond acceptor for the remaining two bonds. When an extra proton is introduced into this hydrogen bonded network of water, a hydronium ion (H_3O^+ ; oxygen with three equivalent protons) is generated. This hydronium ion is solvated by three water molecules, forming three strong hydrogen bonds, and this structure is termed an Eigen ion (H_9O_4^+). In order to transfer the proton from the hydronium ion to one of its neighboring water molecules, an intermediate structure known as a Zündel ion (H_5O_2^+) must form between the hydronium ion and a water molecule, which involves them sharing a proton [1–9]. When the proton is transferred to the neighboring water molecule, the neighboring water molecule then becomes a hydronium ion. Proton transport does not require the net diffusion of a proton, but instead takes place according to the Grotthuss mechanism involving the making and

A. Chaudhari (✉) · G. A. Meraj
School of Physical Sciences,
Swami Ramanand Teerth Marathwada University,
Nanded 431 606, India
e-mail: ajaychau5@yahoo.com

S.-L. Lee
Department of Chemistry and Biochemistry,
National Chung-Cheng University,
Ming-Hsiung,
Chia Yi 621, Taiwan

breaking of hydrogen bonds. The proton transfer mechanism can lead to considerable distortion of the geometry of the hydrogen bonded network of water. Given the importance of the proton transfer mechanism, it is desirable to gain more information on it using computational methods. There have already been extensive investigations of extra protons and hydroxide ions in the water system [3, 7, 10–64]. Determining the details of the proton transfer mechanism is a difficult task, both experimentally and theoretically. Although a number of experimental and theoretical investigations have been carried out to study the solvation of hydronium ions and the proton transfer mechanism, several properties of the proton transfer mechanism remain unclear [3, 6, 8–64]. One of these is the energetics of the proton transfer mechanism: how do the different interaction energies change during the proton transfer process? To the best of our knowledge the changes in many-body energies (two-body, three-body, four-body, etc.) that occur during the process of proton transfer from a hydronium ion to a neighboring water molecule in its first solvation shell have not been studied so far. Thus, the goal of the current work was to shed further light on the proton transfer mechanism by studying the changes in many-body energies that occur during the proton transfer process. The aim of this study was to obtain the potential energy surface and the many-body energies for the proton transfer mechanism and to study the changes in these many-body energies during the proton transfer process. This paper is organized as follows. The next section gives computational details. Results are presented and discussed in the “Results and discussion” section. Conclusions are inferred in the last section.

Computational details

First, the symmetric hydrated hydronium ion was optimized at the B3LYP/6-311++G** and MP2/6-311++G** levels [65–72]. All of the calculations were performed using the Gaussian 03 software package [73]. The potential energy surface for the proton transfer process was then obtained by varying the distance between one of the protons bound to the hydronium ion and the oxygen atom of the corresponding hydrogen-bonded water molecule. The bond distance between the proton and the oxygen atom of the acceptor water molecule was varied from 1.577 Å to 1.250 Å. This bond distance was kept fixed during optimization. The structure was optimized for each bond length, and many-body analysis was applied to obtain the many-body energies for each optimized structure [74–83]. Here, the extra proton was always assigned to the donor water molecule. Even for the shortest distance of 1.250 Å between the proton and the oxygen atom of the acceptor

water molecule, the distance between the proton and the oxygen of the donor water molecule is 1.155 Å, which indicates that the proton still belongs to the donor water molecule. If the proton is closer to the oxygen of the acceptor water molecule than that of the donor, the acceptor water molecule then becomes a hydronium ion. In this study there was no point at which the proton was closer to the acceptor than the donor, so we didn't need to change the definition of the system.

Many-body energies for the hydrated hydronium ion complex are obtained using the many-body analysis technique [74–83]. The total energy of the complex is decomposed into the relaxation energy and many-body energies as follows:

$$\begin{aligned} \Delta E &= E(1234) - \{E_A + nE_W\} \\ &= \sum_{i=1}^n E(i) - \{E_A + nE_W\} && \text{(relaxation energy)} \\ &+ \sum_{i=1}^{n-1} \sum_{j>i}^n \Delta^2 E(ij) && \text{(Two-body energy)} \\ &+ \sum_{i=1}^{n-2} \sum_{j>i}^{n-1} \sum_{k>j}^n \Delta^3 E(ijk) && \text{(Three-body energy)} \\ &+ \Delta^4 E(1234) && \text{(four-body energy)} \end{aligned} \quad (1)$$

where $E(i)$, $E(ij)$, $E(ijk)$ and $E(1234)$ are the energies of the various monomers, dimers, trimers, and the tetramer in the complex, and E_A and E_W are the energies of the isolated hydronium ion and water molecules, respectively. The pairwise two-body interaction energies and the higher three-body and four-body interaction energies are defined as

$$\Delta^2 E(ij) = E(ij) - \{E(i) + E(j)\} \quad (2)$$

$$\begin{aligned} \Delta^3 E(ijk) &= E(ijk) - \{E(i) + E(j) + E(k)\} \\ &- \{\Delta^2 E(ij) + \Delta^2 E(ik) + \Delta^2 E(jk)\}, \end{aligned} \quad (3)$$

$$\begin{aligned} \Delta^4 E(1234) &= E(1234) \\ &- \{E(1) + E(2) + E(3) + E(4)\} \\ &- \left\{ \begin{array}{l} \Delta^2 E(12) + \Delta^2 E(13) + \Delta^2 E(14) \\ + \Delta^2 E(23) + \Delta^2 E(24) + \Delta^2 E(34) \end{array} \right\} \\ &- \left\{ \begin{array}{l} \Delta^3 E(123) + \Delta^3 E(124) + \Delta^3 E(134) \\ + \Delta^3 E(234) \end{array} \right\} \end{aligned} \quad (4)$$

The BSSE-corrected energy of the subsystem ($ijkl$) is evaluated in the full basis of a larger system (1234), and

denoted by the term $E(ijk|1234)$. Accordingly, the n -body terms are replaced with the BSSE-corrected ones:

$$\Delta^2 E_C(ij) = E(ij|1234) - \{E(i|1234) + E(j|1234)\} \quad (5)$$

$$\begin{aligned} \Delta^3 E_C(ijk) = & E(ijk|1234) \\ & - \{E(i|1234) + E(j|1234) + E(k|1234)\} \\ & - \left\{ \begin{aligned} & \Delta^2 E(ij|1234) + \Delta^2 E(ik|1234) \\ & + \Delta^2 E(jk|1234) \end{aligned} \right\} \end{aligned} \quad (6)$$

$$\begin{aligned} \Delta^4 E_C(1234) = & E(1234) - \left\{ \begin{aligned} & E(1|1234) + E(2|1234) \\ & + E(3|1234) + E(4|1234) \end{aligned} \right\} \\ & - \left\{ \begin{aligned} & \Delta^2 E(12|1234) + \Delta^2 E(13|1234) \\ & + \Delta^2 E(14|1234) + \Delta^2 E(23|1234) \\ & + \Delta^2 E(24|1234) + \Delta^2 E(34|1234) \end{aligned} \right\} \\ & - \left\{ \begin{aligned} & \Delta^3 E(123|1234) + \Delta^3 E(124|1234) \\ & + \Delta^3 E(134|1234) + \Delta^3 E(234|1234) \end{aligned} \right\} \end{aligned} \quad (7)$$

All energies reported in this work are BSSE corrected.

Results and discussion

We first optimize the geometry of the symmetric hydrated hydronium ion. This is the first point on the potential energy surface of the proton transfer mechanism. After optimizing the geometry of the symmetric hydrated hydronium ion, we then optimize the geometry of the hydrated hydronium ion for different fixed bond lengths between the extra proton and the oxygen of the acceptor water molecule. In the symmetric hydrated hydronium ion, the hydronium ion forms three strong hydrogen bonds with three water molecules in its first solvation shell. One of these bond lengths was varied. Geometric optimization was performed for each bond length (fixed). We first discuss the symmetric hydrated hydronium ion and the many-body interaction energies for this structure. Then we discuss the changes in the many-body energies that occur during the proton transfer process.

In the following discussion, values with and without parentheses are obtained at the MP2/6-311++G** and B3LYP/6-311++G** levels, respectively. Figure 1 shows the minimum energy structure of the symmetric hydrated hydronium ion with a BSSE-corrected total energy of

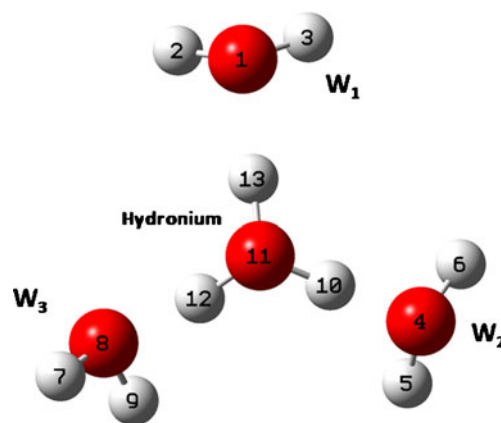


Fig. 1 Hydrated hydronium ion optimized at the B3LYP/6-311++G** level

−306.364903 (−305.605866) Hartrees. The hydronium ion forms three strong hydrogen bonds with three water molecules in its first solvation shell. Each hydrogen bond is 1.577 (1.555) Å in length. The three HOH angles for the solvated hydronium ion are 105.8° (104.2°), and these angles are 109.8° (106.9°) for the isolated hydronium ion. This indicates that the three HOH angles for isolated hydronium decrease by 4° (2.7°) upon solvation. The three O–O distances between the hydronium oxygen and the oxygen atom of each water molecule are found to be 2.577 (2.555) Å. In the isolated hydronium ion, the O–H bond lengths are found to be 1.027 (1.017) Å, whereas they become 1.023 (1.015) Å after solvation. The three O–H bond lengths in the hydronium ion are also shortened by 0.004 (0.002) Å upon solvation. The two O–H bond lengths for isolated water molecules are equal and are 0.962 (0.959) Å in length. However, for all three water molecules solvating the hydronium ion, these two O–H bond lengths are not equal: they differ by 0.012 (0.011) Å. Both of the O–H bond lengths for the solvating water molecules are longer than the O–H bond lengths for the isolated water molecule. The HOH angle for an isolated water molecule is 105° (103.5°), whereas that for a water molecule in a cluster is 105.8° (104.2°)—an increase of 0.8° (0.7°).

Table 1 shows the many-body interaction energies for the symmetric hydrated hydronium ion hydrogen-bonded complex. From Table 1, there is an attractive interaction between the hydronium ion and the three water molecules in its first solvation shell, and the hydronium–W₁, hydronium–W₂ and hydronium–W₃ interaction energies are almost equal at the MP2 as well as the B3LYP levels. These energies are −8 kcal mol^{−1} and −5.4 kcal mol^{−1} at the B3LYP/6-311++G** and MP2/6-311++G** levels of theory, respectively. This is because the hydronium ion forms three equal and strong hydrogen bonds with these three water molecules, and these hydrogen bonds are each 1.577 (1.555) Å in length. The bond lengths between the

Table 1 Many-body energies for the hydronium ion–water₃ hydrogen-bonded complex, obtained using the B3LYP/6-311++G** and MP2/6-311++G** levels

Energy	B3LYP/6-311++G**	MP2/6-311++G**
Relaxation energy (kcal mol ⁻¹)	-1.93	-7.89
Two-body energies (kcal mol ⁻¹)		
HDN–W ₁	-7.99	-5.40
HDN–W ₂	-8.02	-5.41
HDN–W ₃	-7.99	-5.40
W ₁ –W ₂	1.25	1.22
W ₁ –W ₃	1.26	1.22
W ₂ –W ₃	1.27	1.21
Three-body energies (kcal mol ⁻¹)		
HDN–W ₁ –W ₂	-2.74	-2.47
HDN–W ₁ –W ₃	-2.74	-2.47
HDN–W ₂ –W ₃	-2.74	-2.46
W ₁ –W ₂ –W ₃	-0.12	-0.13
Four-body energy (kcal mol ⁻¹)		
HDN–W ₁ –W ₂ –W ₃	-1.67	-3.40
Total two-body energy (kcal mol ⁻¹)	-20.22	-12.55
Total three-body energy (kcal mol ⁻¹)	-8.33	-7.58
Binding energy (kcal mol ⁻¹)	-32.14	-31.44
BSSE-corrected total energy (Hartree)	-306.364902	-305.605866

All energies are BSSE corrected. HDN is the hydronium ion and W_{*i*} denotes the *i*th water molecule in the complex according to Fig. 1

hydronium oxygen and the oxygens of the three water molecules are also equal. The hydronium–W₁, hydronium–W₂ and hydronium–W₃ interaction energies make a significant contribution to the total two-body energy of the hydrated hydronium complex at both levels of theory. On the other hand, the interaction energies between any pair of water molecules are repulsive for this complex, and the W₁–W₂, W₁–W₃ and W₂–W₃ interaction energies are also equal. The difference between the water–water interaction energies obtained at the B3LYP and MP2 levels (1.26 vs. 1.22 kcal mol⁻¹) is only small. As well as the two-body energies, the three-body energies also make a significant contribution to the binding energy of the hydrated hydronium hydrogen-bonded complex at both levels. All four three-body energies are attractive in nature. The largest contributions to the total three-body energy of the complex come from the hydronium–W₁–W₂, hydronium–W₁–W₃ and hydronium–W₂–W₃ three-body energies, which are also equal. In contrast to the significant difference in the hydronium–water two-body interaction energies at the MP2 and B3LYP levels, the difference between the hydronium–water–water and the water–water–water three-body interaction energies is very small at these two levels. At both levels of theory, the W₁–W₂–W₃ interaction energy is negligible compared to the hydronium–water–water interaction energies. The total three-body energy for this complex is -8.33 (-7.58) kcal mol⁻¹. Table 1 also shows that although the hydronium–W₁–W₂–W₃ four-body energy is low compared to the total two-body and total three-body energies, it is not negligible at either

level. The relaxation energy, which measures the degree of strain that drives the structural distortion of an individual molecule in a complex, is also not negligible, and it contributes significantly to the binding energy of a complex. The contributions of the relaxation energy and the four-body interaction energy to the binding energy of the complex are greater at the MP2 level than at the B3LYP level.

From many-body energies (two-body, three-body and four-body interaction energies), it can be said that when hydronium ion is one of the molecules included in the two-body, three-body and four-body terms, the interaction energies are higher and are attractive in nature, whereas when the hydronium ion is not included in the many-body terms, the energies are low at the B3LYP and MP2 levels. The contributions of the two-body, three-body, four-body and relaxation energies to the binding energy of the hydrated hydronium ion hydrogen-bonded complex were 62.9 (39.9) %, 25.9 (24.16) %, 5.2 (10.81) % and 6 (25) %, respectively.

The changes in the two-body and three-body energies during the proton transfer process are shown in Fig. 2. The hydronium–W₁, hydronium–W₂ and hydronium–W₃ interaction energies remain attractive, whereas those between water molecules (W₁–W₂, W₁–W₃ and W₂–W₃ interaction energies) remain repulsive during the proton transfer process at the B3LYP and MP2 levels. On comparing the hydronium–W₁, hydronium–W₂ and hydronium–W₃ interaction energies, it can be seen that the changes in these three energies are not uniform. The hydronium–W₂

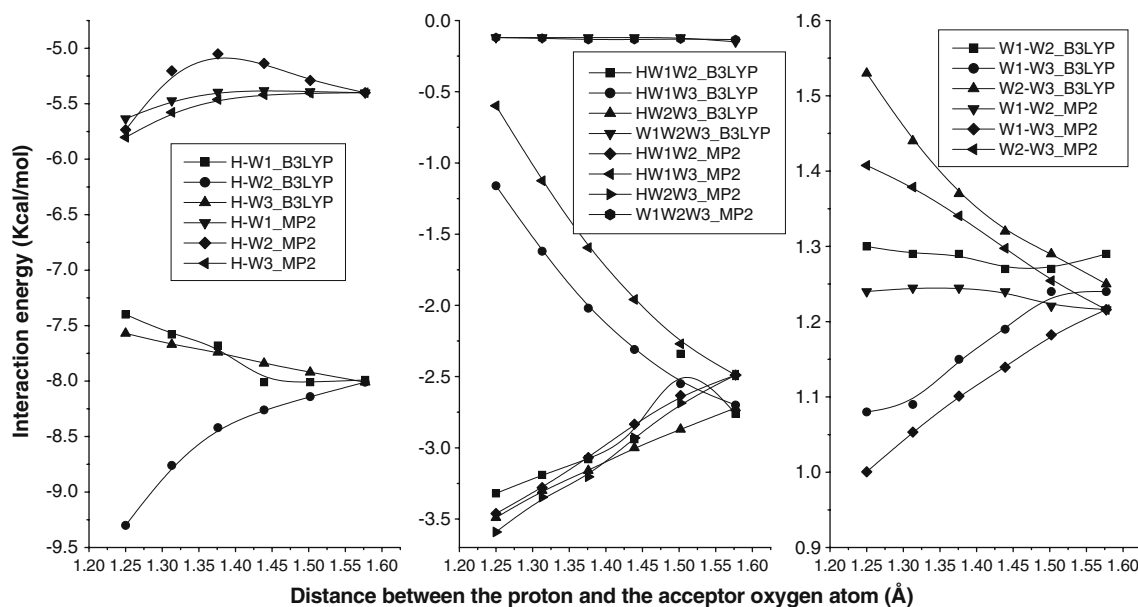


Fig. 2 Changes in the two-body and three-body energies during the proton transfer process

interaction energy changes more than the hydronium– W_1 and the hydronium– W_3 interaction energies at both levels. The hydronium– W_2 interaction energy is more attractive when the proton is 1.250 Å from the oxygen atom of the acceptor than it is for the symmetric hydrated hydronium structure. Similarly, the changes in the W_1 – W_2 , W_1 – W_3 and W_2 – W_3 interaction energies between water molecules are also not uniform at either level. There is almost no change in the W_1 – W_2 interaction energy during the proton transfer process, whereas the changes in the W_1 – W_3 and W_2 – W_3 interaction energies are large compared to the W_1 – W_2 interaction energy at both levels. The largest change in interaction energy is obtained for the W_2 – W_3 interaction energy among the three energies between water molecules at the B3LYP and the MP2 levels. As the proton moves away from the hydronium towards one of the water molecules in the first solvation shell of hydronium, the W_2 – W_3 interaction energy becomes more repulsive than that for the symmetric hydrated hydronium ion structure. On the other hand, the W_1 – W_3 interaction energy becomes less repulsive than that in the symmetric hydrated hydronium ion structure at both levels.

On comparing the three three-body energies (hydronium– W_1 – W_2 , hydronium– W_1 – W_3 , hydronium– W_2 – W_3), it can be seen that the hydronium– W_1 – W_3 interaction energy changes more than the hydronium– W_1 – W_2 and hydronium– W_2 – W_3 interaction energies at both levels of theory. All three energies remain attractive in nature during the proton transfer process. The hydronium– W_1 – W_3 interaction energy becomes less attractive during the proton transfer process, whereas the hydronium– W_1 – W_2 and hydronium– W_2 – W_3 three-body energies become more attractive than

that in the symmetric hydrated hydronium ion structure. There is almost no change in the W_1 – W_2 – W_3 three-body energy during the proton transfer process at the MP2 and the B3LYP levels.

The binding energy and relaxation energy during the proton transfer process are shown in Fig. 3. The BSSE-corrected total energies show that when proton moves away from the hydronium ion the structure becomes less stable. The symmetric hydrated hydronium ion structure is more

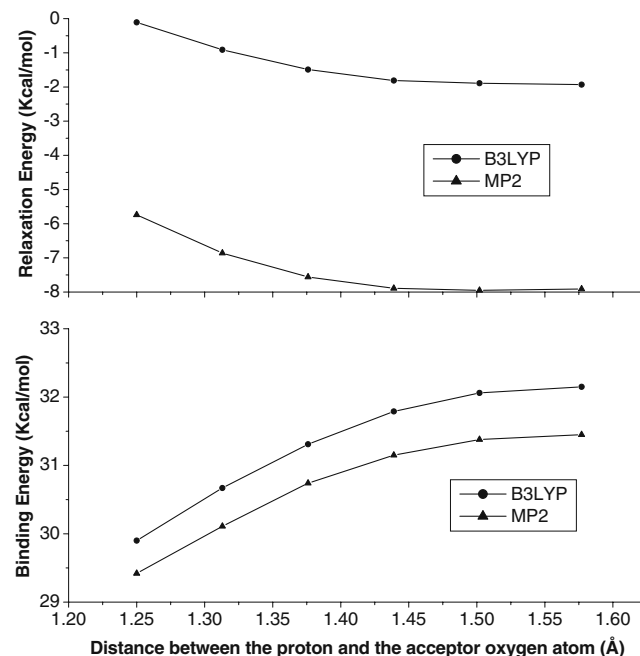


Fig. 3 Changes in the binding energy and the relaxation energy during the proton transfer process

stable than the other structures studied here. This can also be seen from the binding energy of the complex, as plotted in Fig. 3. The symmetric hydrated hydronium ion structure has a maximum binding energy of $32.14 \text{ kcal mol}^{-1}$. The binding energy of the complex decreases from $32.14 \text{ kcal mol}^{-1}$ to $29.9 \text{ kcal mol}^{-1}$ during the proton transfer process. The relaxation energy remains attractive throughout the proton transfer process. As the proton moves away from the hydronium ion, the relaxation energy becomes less attractive at both levels of theory used here.

The % contributions of the many-body energies to the binding energy of the complex at the MP2/6-311++G** level are shown in Fig. 4 for all of the structures studied here. In all of the structures, the two-body energies contribute the most to the binding energy of the respective structure. During the proton transfer process, the % contribution of the total two-body energy to the binding energy of the complex increases from 62.9 to 68.09% (39.9 to 45.95%), and that of the total three-body energy increases from 25.9 to 27.09% (24.16 to 26.17%). There is a large change in the % contribution from the relaxation energy, from 6 to 0.36% (25.10 to 19.75%), during the proton transfer process. On the other hand, there is a change in the % contribution of the total four-body energy from 5.2 to 4.48 % (10.81 to 8.1%) during the proton transfer process.

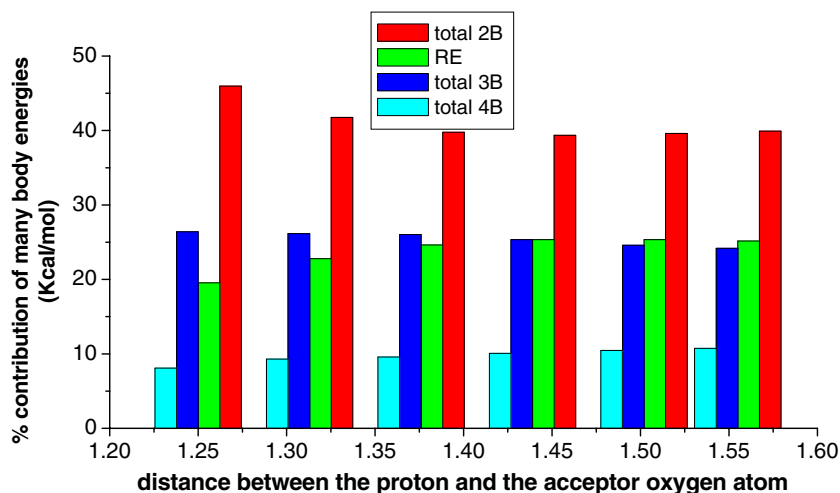
Kulkarni et al. [82] and Maheshwari et al. [84] studied water clusters using ab initio and DFT methods. They developed an automated algorithm for many-body interaction analysis, and used this algorithm to study $(\text{H}_2\text{O})_n$ and formamide- $(\text{H}_2\text{O})_n$ ($n=12, 16, 24, 28$), subsequently reporting many-body energies for these homo- and heteroclusters. On comparing the many-body energies obtained in this work with those obtained for water clusters, it can be said that the total two-body, total three-body and total four-body interaction energies are attractive, similar to those in the water clusters. However, the relaxation energies are

repulsive at both the B3LYP and the MP2 levels, in contrast to the attractive relaxation energies for the homo- as well as heteroclusters reported by Kulkarni et al. [82]. As also observed by Kulkarni et al. for water clusters, the BSSE-corrected two-body interaction energy per water molecule gradually increases during the proton transfer process, and this growth is very small, as observed in water clusters. On comparing the % contributions of the many-body energies from this work with those for water clusters, it can be said that introducing an extra proton into a hydrogen-bonded water cluster changes the % contributions of the many-body energies significantly. The contribution of the total two-body and three-body terms for a water cluster is more than 95%, whereas it was found to be 88% at the B3LYP level and 64% at the MP2 level in our work. The four-body energy component for a water cluster is around 1.5%, whereas in this work it was found to be higher: 5.19% at the B3LYP level and 10.81% at the MP2 level.

Conclusions

The changes in the many-body energies during the proton transfer process in an aqueous system have been studied at the B3LYP/6-311++G** and MP2/6-311++G** levels of theory, and the potential energy surface of the proton transfer process was obtained. Many-body analysis was applied to each structure on the potential energy surface to study the contributions of the many-body energies to the binding energy of these complexes. Similar changes in the many-body energies during the proton transfer process were observed at the MP2 and B3LYP levels. For all the structures studied here, the total two-body energy contributes more to the binding energy of the complex than higher-body energies do. The % contributions from the total two-body energy and the total three-body energy to the binding energy increase

Fig. 4 % contributions of the many-body energies to the binding energy of the complex during the proton transfer process at the MP2/6-311++G** level



during the proton transfer process, and that from the relaxation energy decreases during the proton transfer process. The contribution from the four-body energy is also not negligible.

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