The electron density delocalization of hydrogen bond systems

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**ABSTRACT**

Recent experimental and theoretical researches have gradually proved that hydrogen bond (H-bond) interactions are not simple traditionally considered electrostatic interaction. Instead, they involve electron density delocalization. In this work, we outline the studies of electronic structures of the H-bond systems in water systems and biological organic molecules systems. Theoretical researches based on the first-principles method have found important evidences for electron density delocalization in H-bond region. Topological analysis based on natural bond orbital (NBO) analysis proves that during the formation of the H-bonds, electrons transfer from B orbitals to A–H anti-bond orbitals. Energy decomposition analyses revealed that the delocalized electronic structures show strong relations with orbital interactions. Moreover, penetrating molecular orbitals (MOs) are proved to contribute to the electron density delocalization of the H-bonds, and the quantitative contributions for such MOs could be obtained with the electronic density projected integral (EDPI) method. The electronic delocalization and the corresponding penetrating MOs could be visualized in water clusters, based on the first-principles method. These researches open a new sight for understanding the electronic structures of H-bonds from atomic level, and even contribute to further controlling proton tunneling as well as charge and energy transfer processes.

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**Introduction**

Hydrogen bond (H-bond) plays many important roles in physics, chemistry and life sciences. According to the IUPAC definition [1,2], in a typical X–H···Y H-bond system, H-bond is an attractive interaction between a hydrogen atom from a molecule or a molecular fragment X–H in which X is more electronegative than H, and an atom or a group of atoms in the same or a different molecule, in which there is evidence of bond formation. Generally, in the H-bonded systems, H atom could be found to be partially positively charged due to the polarization effect of the X atom, while X atom turns out to be partially negatively charged atoms, such as the most typical O, F, or N atoms.

It is of general expectation that the most typical H-bond could be found in water systems. Besides, the double helix structures of DNA also rely on the H-bond interaction. Even between the functional groups of the organic molecules containing O, F, N atoms could the H-bonds exist. Stronger or weaker H-bonds could also occur in other systems, for example the strong systems HF$_2^−$ and H$_2$O$_2^{+1n}$ [3] and weak ones CH···OH$_2^+$ [4]. As one of the most important interactions, the properties of H-bonds have long been studied [5–42], such as bond strength dependency [43–45], proton tunneling feature [46–49], dynamics properties [50,51], surface hydrophilia [52–58], and spectroscopy properties [59–61]. Many substances and interactions of life depend greatly on the H-bond interaction, such as the formation of proteins and DNA, and the interactions between these molecules and water [62,63].

The traditional recognitions into the H-bonds are dipole–dipole forces or essentially electrostatic interactions [64,65]. However, some works have reported that the donor–acceptor orbital interactions between electron long pairs with X–H anti-bond show an almost same magnitude contribution to the H-bond strength as electrostatic ones, which are different properties of H-bond [66–68]. Meanwhile, anion–anion and cation–cation-type complexes were revealed to have the H-bond
feature, despite the large electrostatic distracting effect, which could be overcome by charge-transfer force [69]. All these studies show that, H-bonds are not only pure electrostatic interaction, but it is generally concluded that H-bonds in a typical X–H···Y system are involved with electron transfer from lone-pair orbitals of Y atom to the anti-bond orbital of X–H. Hence, further exploring the mechanism of H-bond is of great necessity. More recent researches, including our previous works, revealed that orbital interactions play non-negligible roles in the H-bonds. Meanwhile, real-space penetrating molecular orbitals (MOs) crossing the H-bond area were discovered to contribute to the H-bond. The electron density-related researches have long been paid attention since last century [70], which is the most measureable one [71–75] among available properties based on the wavefunction descriptors of H-bonds. Therefore, studying the electron density delocalization feature and its contribution to the H-bond interaction is needed. In this review, we give a concise overview of the recent development of theoretical and experimental researches into the H-bond. The progresses of the researches towards the electron delocalization in typical H-bond systems are also introduced. We hope these studies could provide more insight into the understanding of H-bond mechanisms.

**Methods**

The theoretical researches into the H-bonds have long been developed over the past century. First-principles methods including *ab initio* and density functional theory (DFT), classical force field model, semi-classical model, and also the combination of these calculations have been used in studying the H-bond systems. From these approaches, first-principles methods are widely applied in the recent works, which have provided a lot of progresses in understanding the mechanism of H-bonds. Especially, Hobza et al.’s works discovered that H-bonds actually belong to low-order electronic correlation, instead of normal intermolecular stacking interaction [76,77], which are inspiring for further investigations with first-principles methods, including DFT and *ab initio* based the second-order perturbation theory.

DFT calculations are widely used in many H-bond systems. Compared with *ab* initial calculations, DFT levels could provide higher leveled real-space MOs with energy eigenvalues, whose properties could be more easily observed in the experimental approaches [78]. Among the DFT methods, the hybrid-DFT, such as PBE0 [79–81] and B3LYP [82], could provide high-quality electronic density results. Recently, dispersion is also commonly used in DFT calculation, which is important for correcting the geometry structure. However, it will not obviously influence the quality of electron density. Apart from the geometric optimization, electron density analyses, molecular orbital analyses as well as energy decomposition analyses are also widely used tools to study bonding interactions. Quantum theory of atoms in molecules (QTAIM) theory [83,84] is also an important topology-based method to study electron density properties of H-bonds.
Combined with orbital analyses, the quantitative contribution of certain orbitals to the H-bond could be revealed. Meanwhile, the energy decomposition is one of the most important approaches to analyze the molecular interaction. Among the current energy decomposition, a main stream method has been established according to the works of Morokuma [85] and Rauk et al. [86], in which the interaction energy could be decomposed into electrostatic interaction term, Pauli repulsion term, orbital interaction term, and dispersion term. Different contribution of these terms, especially the electrostatic and orbital interaction energies, could roughly determine the type of interaction, which is helpful for studying the mechanism of bonding.

**Electronic density delocalization**

**The development of recognitions into H-bond**

The concept of the H-bond could date back to 1920s. Conventional understanding of H-bond was one kind of relatively strong intermolecular dipole–dipole interaction or that showing essentially electrostatic character [87–98]. However, since latter part of the last century, some researches have provided challenging results that are against such traditional definition [69,99,100]. In 1975, Morokuma et al. reported a theoretical study based on decomposing the interaction and the corresponding electron distribution of water dimer in order to further investigate the detailed interaction mechanism of H-bonds [99]. The results show accumulations of electronic density in the intermolecular region, which were mainly flowed from the lone-pair O atom of the proton–acceptor molecular to the intermolecular region, indicating covalent-like attractive force. These studies support the different aspects of H-bond as partial covalent or fractional chemical bonding. Since 2015, our group has carried out energy decomposition analyses, orbital analyses, and topology analyses to investigate the intermolecular interaction in water systems. From these approaches, the electronic delocalization between the O atoms of both donor and acceptor water molecules could be further observed, and even clarify the covalent-like feature of H-bond between water molecules [101–105].

Electron density has long been analyzed for studying the properties of interactions between atoms. Specially, electron density based topological analyses have been widely used as a mainstream tool to investigating the close contacts [106], which has been studied in various systems. By taking the advantages of topological analyses, the electron density properties of two-body or even multi-body close contacts can be studied more detailedly.

Natural bond orbital (NBO) analyses can also be introduced for calculating electronic properties of H-bond. Weinhold et al. detailedly investigated the H-bond properties of the H-bond in water dimer by advantages of combining NBO and QTAIM [107]. Taking water dimer (H₂O)₂ as an example, a distinctive intermolecular bond critical point (BCP) could be found between the H-bond O and H atoms. The electron density at the BCP and the natural bond critical
point (NBCP) are 0.025 and 0.030, respectively, which are obviously lower than the covalent bonds as expected. However, NBO decomposition reveals a large contribution in the 10th natural bond orbital (NBO 10), the nature orbital of the H-bond O atom, and NBO 2, the covalent OH bond of the proton donor monomer. Also, there is also evidence for large contribution of OH anti-bond in NBO 70, the OH anti-bond orbital of donor, involved with H-bond. This find is corresponding to Morokuma et al.’s report.

H-bond could be found between many neutral functional groups [108]. Moreover, charge assist hydrogen bond (CAHB) could also be found in the positively or negatively charged systems [109]. For these CAHBs, the charge of the system would strengthen the hydrogen bonding, leading to larger H-bond energies. Then whether the H-bond could exist between functional groups with same charges is of great interest. In 2014, Weinhold and his co-workers has revealed evidences of the anti-electrostatic H-bonds in anion-anion and cation–cation H-bond compounds [69], for example, the [F···HCO$_3$]$^{2-}$ system. The charge transfer from the lone-pair orbital of F anion to OH anti-bond orbitals could be observed from the DFT calculation, as shown in Figure 1(a). Taking the simplest ion–ion H-bond system [B···H–A]$^{2-}$ complex as example, in such closed-shell ion–ion H-bond system, the ion monomers must overcome about 100 kcal/mol energy barrier to reach H-bond distance. However, quantum mechanics indicated that exchange-type covalent-like effect could provide attractive energy to such long-range electrostatic force. According to Weinhold et al.’s results, a relax scan along the H-bond length suggests that there exits an energy well at around 1.81 Å. The second-order interaction energy of this process is 13.25 kcal/mol, while the charge transfer from F$^-$ to HOCO$_2$$^{2-}$ is 0.38 e. Meanwhile, the electron density and Laplacian density at the BCP are 0.0314 and 0.0928, while for NBCP are 0.0361 and 0.0970, respectively. These results are all of reasonable magnitude for the existing of a typical H-bond system. Thus, although the exchange repulsion was found as large as expected, owing to the same positive or negative electron of such compounds located on each of the ions, the interaction within anti-electrostatic H-bonds still satisfy the criteria of its existing. Similar H-bonds could also be found in other systems (see in Figure 1(b)–(f)). This study provides an important evidence for new understanding of H-bonds that H-bond interactions are not only electrostatic interaction. All the analyses above have suggested that the detailed properties of H-bond interaction have been gradually discovered.

**Electronic delocalization in H-bond systems**

Different from the general method quantitative mechanical calculation, Sun et al. reported the understandings of H-bond of water with a conventional model, by solving Laplacian equation [110,111]. More importantly, they directly established the ($H_2O$)$_2$ H-bond model in a pattern shown as Figure 2. It means that for the whole H-bond system, the O: H H-bond interaction should be included, while
the O–H covalent bond must also be considered. This concept of H-bond was regarded as ‘the attribute of water’.

From such a classical perspective, the charge transfer could also be modeled. The H-bond (O:H–O) also gives out the unique properties that the relatively

Figure 1. The $\sigma_{AH}^* \rightarrow \sigma^*_{B}$ NBO interaction in different anti-electrostatic H-bond systems. Notes: The isosurfaces suggested the NBOs of the monomers. The isosurfaces with different colors suggest different direction of charge transfer. The yellow-colored isosurface represent the electron loss and the blue part suggests electron increase. The ball models colored in white, black, blue, red, and yellow represent H, C, N, O, and F atoms. The H-bond well depths and the equilibrium H-bond lengths were listed for each of the systems. Figure reproduced from Ref. [69].
positive charged proton donates its electron to the oxygen atom to form the intramolecular H–O polar covalent bond, while the O:H H-bond is formed by sharing the lone pair O electron of the proton acceptor to the proton donor through polarization effect. However, the Coulomb repulsion between the electron pairs of the oxygen atoms should not be ignored. Instead, the Coulomb repulsion is also the key component of the interaction between the water monomers. The intermolecular and intramolecular bonds would react to the stimulation cooperatively and oppositely in direction and extent, which is vital to the properties of the O:H–O bond.

Actually, such O–O interactions in the water H-bond systems have been paid more and more attention. From an orbital-resolved view towards the water dimer system, a research upon contributions of the MOs to the electron density delocalization has shown a special morphologically penetrating MO in the \((\text{H}_2\text{O})_2\) system that all cross the O–H···O area [105]. In order to figure out the specific quantitative distribution of the MOs, a new method named electronic density projected integrated (EDPI) was introduced. According to the EDPI method, the electron density in the intermolecular region is projected onto a line that linked the X atom and H atom in the typical X···H–Y system. Assuming that the H-bond lies right on the \(y\)-axis, the \(y\)-related function of projected could be obtained, as well as other axis. Moreover, by substituting the electron density of each MO, the distributions for these MOs can thus be obtained, respectively.

Taking the most typical water dimer as an example, two penetrating MOs (HOMO-2 and HOMO-4) have been proved to be probably responsible for the electronic delocalization in the intermolecular region. In order to further find out the detailed contribution of these MOs, the EDPI method could be introduced. The results show that the projected electronic density reached an extreme point at around 1.32 Å, namely the one-dimensional projected critical point (OBCP). In this point, the distribution of each MO could be obtained as Figure 3.

![Figure 2](image)  
**Figure 2.** Segmentation and short-range interactions in an O:H–O bond.  
Note: Figure reproduced from Ref. [110].
From the EDPI results, HOMO-4 plays a relatively dominant role in the electron density delocalization of the H-bond. However, the morphologically penetrating HOMO-2 shows rather similar distribution as those of the non-penetrating MOs. In order to figure this out, density of states (DOS) analyses could be used for more detailed information. DOS analyses are methods to calculate the distributions of electronic state, which could conclude abundant information of energy levels of MOs and contributions of certain atoms, electronic shells or even bases to those states. Also, to analyze the DOS distributions along the H-bond, local density of states (LDOS) could be used. The result shows that HOMO-4 presents high delocalizing feature all through the entire O–H···O system. Meanwhile, for the other penetrating MO, HOMO-2 indicates lesser delocalization distribution. This could be concluded that although HOMO-2 shows penetrating character, it does not involve with as much interaction as HOMO-4. However, EDPI method is currently more suitable for analyzing linear systems, or, otherwise, there could be problems when dealing with complicated ones. Therefore, much more effort should be put into it before being applied to more general applications.

Electron density differences are effective analyses for studying the properties of bonding interactions. By decomposing the electron density differences into detailed interactions, one could obtain more information of the basic mechanism of bonding. Morokuma et al.’s decomposed the interaction energy of water dimer into electrostatic energy, exchange repulsion energy, polarization energy and charge transfer energy (also namely delocalization energy), and the electronic density corresponding to each part could also be obtained, by integrating the different wavefunctions of each part [99]. The electronic attraction part does not

**Figure 3.** Electron density integral of the MOs projected on the H-bond.
Notes: The vertical axis represents the integrated electron density, and the horizontal axis indicates the y-axis on which the O atom of the acceptor is located at y = 0 and the H atom of the H-bond is located at y = 1.93 Å. The vertical dashed line represents the position of the OBCP. Figure reproduced from Ref. [105].
bring in electronic densities difference; the exchange repulsion causes electronic density to localize on the atoms and decrease in the intermolecular region, which results in instability of the whole system; the polarization effects mainly cause electronic density polarized from H-bond proton the rest part of the monomer, and also a relatively small accumulation in the intermolecular region. Meanwhile, the charge-transfer effect could bring in a large increase of electronic density in the intermolecular region. This is the dominant part of the electronic delocalization within H-bond. Our calculations of the electron density difference also revealed that, the orbital interaction causes the electron density increase in the intermolecular region, while the sum of other effects would cause decrease.

Energy decomposition analyses were also used in the \((\text{H}_2\text{O})_2\) system. Our previous work has studied interactions properties of water dimer \[\text{103}\]. Using SAPT treatment, the interaction energy of H-bond can be decomposed into electrostatic, exchange repulsion, induction and dispersion effect. Electrostatic interaction abstracting energy is \(-8.10\) kcal/mol, while the exchange repulsing energy is \(8.04\) kcal/mol. This indicated that the electrostatic effect can only eventually provide \(-0.06\) kcal/mol abstraction effect. Meanwhile, the induction term, which is related to polarization and charge transfer effect, provided a non-negligible \(-1.37\) kcal/mol, taking 28.8% of the total interaction energy. By means of orbital analyses, this could also state that the H-bond is related to the orbital interaction. Meanwhile dispersion effect also contributes a relatively large contribution of \(-2.41\) kcal/mol.

So far, theoretical approaches for observing the electronic density of H-bond have been well established. However, experimental approaches into the electronic density on H-bond had little development. Direct observation of the electronic density of H-bond has seldom been carried out until 2008. T. Kumagai et al. uses a scanning tunneling microscope to investigate water dimer bound on \(\text{Cu}(110)\) surface \[\text{112}\]. A large isotope effect was observed, indicating quantum tunneling effect between the monomers, while the donor-substrate stretching mode assists the interchange tunneling.

Later in 2013, a real-space observation to H-bonds of 8-hydroxyquinolines (8-hq) on \(\text{Cu}(111)\) substrate was carried out, through noncontact atomic force microscopy (NC-AFM) \[\text{113}\]. The results presented that the electron density could be found delocalized within the H-bond region by AFM frequency shift image. For the NC-AFM method, the CO-functionalized tips is deployed to detect the 8-hq molecules placed on the \(\text{Cu}(111)\) substrate. The whole system was at liquid He temperature, under which the 8-hq molecules could stay on the surface. From the AFM image, the frequency shift could be seen along the molecular structure, which indicated the existing of relatively strong short-ranged Pauli repulsion interaction. Such image of frequency shift could not be seen between the substrate Cu atoms. Compared with the theoretical calculation, the presentation of such frequency shift are of high relation with the electron density image. Meanwhile, while detecting the small clustered 8-hq molecules, the AFM images showed
similar high signal where the chemical bond is located, as expected. However, a minor but obvious distribution of the signal could also be observed where H-bond forms between the molecules, performing a bonding-like feature. Therefore, such NC-AFM observation could see the electron density delocalization of the H-bond between 8-hq molecules. The NC-AFM method provides inspirations for experimental observation on the electronic structure, and contributes to the study of bonding interactions.

Actually, scanning tunneling microscope (STM) method has been well developed for observing electronic structures. A recent article has revealed the HOMO and LUMO of water molecules on Au(111) at 5 K [114]. Similar method could also be applied to detect proton tunneling through the H-bonds. An experimental research detected the cyclic water tetramer with Cl-terminated tips by means of STM technology. The results show that when the height of tip above the substrate reduces, the chirality of water tetramer would switch [115]. More recently, another research has also observed double proton tunneling in Porphycene molecule. The height of STM tip could also affect the tunneling property [116]. These studies not only provide a possibility for controlling and manipulating the proton tunneling, but also bring about new insight for direct observing the covalent-like properties of H-bonds.

More recently, Shigeki Kawai et al. also adopted a direct quantitative measurement of H-bond, using AFM, the outmost H atom of propellane molecules was found to form weak C=O···H–C H-bond with CO tip [117]. The result revealed that high frequency shift would present when the CO tip could possibly form H-bond with the outmost C–H parts, while potential energy analyses shows that such C=O···H–C H-bond is just above the onset of Pauli repulsion.

The electron density delocalization effect could also be found in the clusters, and the simplest but the most typical ones should be water clusters. Our previous works studied the cyclic water rings with 3–6 monomers, and revealed the electron density delocalization features [101,102]. For these water clusters, the cyclic structures have the lowest energy, making them the most stable one among their own isomers [118,119]. In these clusters, the energy level diagrams of MOs are listed in Figure 4, in which the penetrating MOs are colored in red. Such penetrating MOs are found to be composed of both O and H atomic orbitals with delocalized electronic densities. Morphologically, such delocalization is present near the traditional hyper conjugation [120,121]. However, it is actually involved with relatively strong electron delocalization. The numbers of the monomers were also found to influence such delocalization: as the number increases, the electron density would gradually become more localized on the monomers. Thus, for \( n = 5 \) cyclic water ring, the electron density shows nearly no contribution to the center part of the system, so as \( n = 6 \). By means of the NBO with natural atomic orbital (NAO) approach, the detailed contribution could be investigated. The main contribution of the penetrating MOs was found to be formed mainly by HOMO-1 and HOMO-2
However, not all of these clusters have proper H-bond angle, especially for $n = 3$ \cite{122,123}. Therefore, the how these clusters remain stable is of interest. For $n = 3$ and $n = 4$ cases, the electron density delocalization of the penetrating MO are large enough that the center of the circle are covered. This is due to the relatively high planar structure of these clusters. As for $n = 5$ and $n = 6$ cases, such delocalization decreased as the number of monomer grows. It should be noticed that the average bonding energies of $(\text{H}_2\text{O})_n$ for $n = 3, 4, 5, 6$, are 5.59, 7.73, 8.03, and 8.20 kcal/mol, respectively. They actually become larger as $n$ increases, which do not reflect direct influence of electron density delocalization. This is because the bonding energies are obtained from complicated combined effect, which included the effect of molecular orbitals. While for $n > 6$ cases, the delocalization would be too weak to keep the stability of the cyclic structure of the clusters. Meanwhile, the energies of the penetrating delocalized orbital energy also go up as $n$ increases. These results could explain that the penetrating orbitals with delocalized electron density are important in the stability of the cyclic structure. Meanwhile, the energy decomposition of the interaction energy shows that the orbital interaction takes more than 30% of the total attractive energy, suggesting that H-bond is probably related to its covalent-like feature. Similar covalent-like features have been shown in other H-bond systems \cite{124}.

Meanwhile, the electrostatic potential analyses also show that the electron delocalization in the central region could also determine the stability of the water ring.

Figure 4. Delocalized penetrating molecular orbitals of cyclic water rings with $n = 3$–6. The red lines suggest the penetrating MOs pictured below, and the corresponding MO labels are marked aside.
Note: Figure reproduced from Ref. [102].
As the n increases, the delocalization in the center region gradually decreases. The boundary would finally appear when \( n = 5 \), which means that the interactions in such areas are regarded as weak ones. Electron density difference could also present the delocalization feature, which could be adopted for confirming the differences found in the orbital delocalization. As expected, the electronic density decreased at the H-bond H atoms, and accumulated in the intermolecular regions. As n increases, the electron density changes in the center region would also decreases. Moreover, the reduced density gradients (RDG) and nuclear independent chemical shift (NICS) also indicated the delocalization decreases as the monomers increases. All the results above revealed that the stability of the cyclic water clusters is highly dependent on the electron delocalization. As the number of the monomers increases, the electron delocalization was reduced, thus making the stability frustrated.

Actually, the water molecules in nature are usually in bulk environment. However, such huge systems are not able to be fully simulated by the current calculation resources. Therefore, it is necessary to investigate relatively small systems that could reflect the properties of water in nature. For \( n > 6 \) water clusters, three-dimensional structures are preferred than the planar or quasi-planar structures. Specially, bilayer cyclic water prisms could also exist. Our previous work has revealed the electron structure of the \((\text{H}_2\text{O})_{2n}\) \([49]\). The results showed that the delocalized MOs would exist not only within both layers, but also between the layers. This could prove the important role the electron density delocalization plays in the configuration of such systems.

Due to the hybridization pattern of the O atom, water molecules are able to form up to 4 H-bonds with other molecules. Two of them are proton donor, while the other two are proton acceptor. Thus, in large water clusters, certain water monomer with 4 H-bond could be obtained. Such water monomers could be named centrally for-coordinated water (C4CW). Previous studies have reported the structure of larger water clusters \([125–130]\). For \( n > 6 \) cases, all the water monomers would form the surface of the cluster, until it comes \( n = 17 \) or more, when stable structures with odd-numbered molecules are C4CW clusters. One exception was found by the recent experimental observations tables for \( n = 20 \), which is also C4CW one \([131]\).

Therefore, our previous work studied the typical C4CW structures with the \( n = 17, 19, 20, 21, 23 \) and \( 25 \), and revealed the quantum effect in such systems \([104]\). For the convenience of statement, the whole systems were divided into the C4CW, the nearest neighbor four waters (NN4W) of the C4CW, and the rest part. As shown in Figure 5, the electron density difference results show that, between the C4CW and the whole rest part, the majority change of electron density were located between C4CW and NN4W. This means that the electronic structure of C4CW would almost only be influenced by NN4W. Therefore, taking C4CW and NN4W as the reference system, it would be of great interest to study the influence of different rest part on it.

Energy decomposition analyses were carried out on the interaction of C4CW and NN4W to reveal the mechanism of the interaction. The interaction energies
could also divide in to three parts, respectively, marked as: $E_{\text{int}}$ (the whole rest parts), $E_{\text{int}(C-4)}$ (the NN4W), $E_{\text{int}(C\text{-rest})}$ (the rest part expect NN4W), indicating the interaction between C4CW and different parts. As the number of $(\text{H}_2\text{O})_n$ grows, the interaction energy could be affected. As expected, the results suggest that $E_{\text{int}(C-4)}$ was always larger than $E_{\text{int}(C\text{-rest})}$, while $E_{\text{int}(C-4)}$ shows the same trend as $E_{\text{int}}$, corresponding to the results of electron density difference analyses. The most interesting feature is that $E_{\text{int}(C-4)}$ and $E_{\text{int}(C\text{-rest})}$ react totally oppositely as $n$ varies. That is to say, a ‘competitive’ mechanism could be found between these two different interactions.

**Summery**

In conclusion, the researches gradually indicate that the H-bond is not the conventionally considered electrostatic interaction, but involves more complicated mechanism. The fact that the electron density delocalized from the lone pair orbital of proton acceptor atom to the anti-bond orbitals of the proton donor molecule has partially suggested the covalent-like feature of the H-bond. Orbital interactions were proved to play a non-negligible role in the total interaction. Penetrating MOs that cross the intermolecular region are proved to contribute to the electron density delocalization, whose detailed quantitative contribution could be obtained by the EDPI method. Electronic density delocalization could also be observed in water clusters. For $n=3–6$ water rings, the electronic density delocalization effect.
is highly related to the stability of the cyclic structures. For larger water clusters, the interaction energies between C4CW and NN4W show competitive effect with those between C4CW and rest parts, while electron density difference also indicated strong correlation between C4CW and NN4W. Furthermore, some recent researches reveal that the core vibration of the protons in H-bond systems might have influences on the strength of H-bonds. The red-shift of the A–H covalent bond suggests the enhancement of the H-bond strength [132–134].

Now that the evidences for electron density delocalization and even the covalent-like feature of H-bond have been reported, further understanding the H-bond from the view of atomic level has been a necessary advance, thus opening a brand-new field in the theoretical and experimental technologies. From this, as a widely attractive issue, the understanding of H-bond mechanism and even the researches on the regulation of H-bond effect will be promoted, thus improving the development of life and material science.

Acknowledgements

The authors would like to acknowledge Dr. Bo Wang, Dr. Ruixia Song, Miss. Sonam Wangmo and Dr. Yan Meng for contributing to the hydrogen bond related works in our group. Also, we would like to thank Prof. Ruiqin Zhang, Prof. Ruhong Zhou and Prof. Changqing Sun for academic discussions. Z. W. also acknowledges the Fok Ying Tung Education Foundation (142001) and the High Performance Computing Center of Jilin University.

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

This work was supported by the National Natural Science Foundation of China [grant numbers 11674123 and 11374004]; and the Science and Technology Development Program of Jilin Province of China [grant number 20150519021JH].

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