

# Establishing a fundamental connection between the covalent component of the hydrogen bonding network and properties of liquid water

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Many remarkable properties of liquid water originate from the ability of water molecules to form hydrogen bond, which is a combination of electrostatic, induction, dispersion and covalent interactions. In this work, we developed an ab initio molecular dynamics method that enabled us to adjust the spatial extent of the covalent component of interactions between water molecules in simulations. We show that for room-temperature liquid water, a seemingly small amount of electron transfer has a profound effect on observable properties of liquid water. In particular, the tetrahedral structure, O-H stretch mode and viscosity are all significantly determined by covalent interactions.

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## INTRODUCTION

Detailed understanding of the physical nature of hydrogen bonding (HB) between molecules in water is essential to unravel origins of the unique properties of this ubiquitous and important liquid. It has been known since the dawn of quantum mechanics that hydrogen bonding is a complex phenomenon that arises from the interplay of several distinct effects: interaction between molecules permanent multipoles (dipoles, quadrupoles, etc.), polarization, dispersion, and donor-acceptor orbital interactions that lead to partial electron transfer between molecules. Recent developments in electronic structure methods have helped to make progress towards solving a long-standing problem of quantifying the individual contributions of these effects to the energy of hydrogen bonding. One last unresolved issue has been the extent of intermolecular charge transfer in hydrogen bonding [1–3]. Natural bond orbital (NBO) analysis[4] and natural energy decomposition analysis [5] suggest that charge transfer (CT) is predominant [6–8] because, if charge transfer is neglected, NBO analysis shows no binding at the water-dimer equilibrium geometry. However, other earlier decomposition methods [9–13] as well as as most recently developed alternatives [14–16] estimated that CT contributes only around 20% of the overall binding energy. After a debate spanning several decades, it is becoming clear that NBO is not optimized to treat intermolecular interactions[3], and covalent donor-acceptor component contributes only a small portion to the overall binding energy between water molecules in small clusters [12, 13, 17–19].

The success of energy decomposition techniques allowed us to look beyond a simple contribution of charge transfer to the interaction energy and to establish a fundamental connection between physical components and the observed properties of water – an area, in which our knowledge remains rudimentary at best. In this work, we coupled ab initio molecular dynamics to a recently developed energy decomposition method for periodic systems

[20] to perform an unprecedented computational study that enabled us to quantify the contribution of the covalent component of hydrogen bonding to the structural, dynamical and spectroscopic properties of liquid water at ambient conditions. We showed that even a seemingly insignificant covalent component of hydrogen bonding has a profound effect on the properties of water.

## METHODS

To isolate the effect of the covalent component of hydrogen bonding on the properties of liquid water, we performed ab initio molecular dynamics simulations using a special version of density functional theory based on absolutely localized molecular orbitals (ALMO)[20, 21]. In ALMO, each molecular orbital (MO) is expanded in terms of the atomic orbitals (AOs) of a fragment containing a certain number of molecules, thus the charge transfer between molecules can easily be adjusted by changing the number of molecules in the fragment. In this work we set the fragment to have only one molecule, totally excluding any charge transfer. **what to say about ALMO MD?**

In order to compare properties of liquid water with and without charge transfer, we look at the system described by ALMO with zero charge transfer, and the system described by normal DFT. The former will be referred to as localized system and the latter delocalized or reference system. We use BLYP functional, TZV2P basis set, and D3 dispersion correction for both systems. The density of these systems are set to be 1.04 g/cm<sup>3</sup> for a MD simulation with NVT ensemble at a temperature of 298K. Since properties like density or pressure can be affected by covalency, we also look at a third system whose density is determined by a NPT simulation at a constant pressure of 1atm. This system will be denoted by high density localized system.

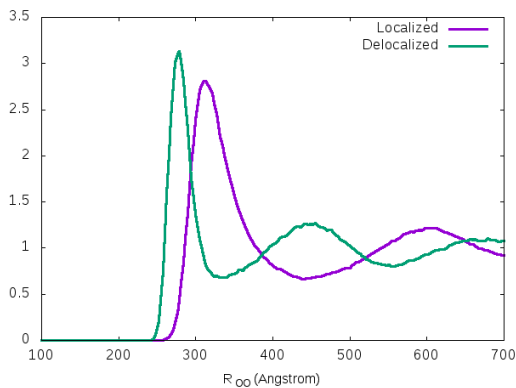


FIG. 1: Oxygen-Oxygen radial distribution function for localized and delocalized water systems. The calculation was done for 125 water molecules with NVT ensemble. The average distance between molecules and the position of the first solvent shell are all larger for the localized system.

## RESULTS

The Oxygen-Oxygen radial distribution function (RDF) is shown in Fig 1. It is clear that the molecules in the localized system turns to be further away, since the interaction between molecules are weaker.

The infrared spectrum for the system is calculated using TRAVIS. Fig 2 shows the infrared (IR) spectrum of the localized and reference systems. For comparison, the IR spectrum of none-interaction water vapor is also shown. The O-H stretch modes of the localized system do not show the broadening and shift due to HBs, as in the delocalized system. Which implies that these modes are very sensitive to covalency, and without covalency, they are very similar to that of the none-interacting molecules. Another difference between the localized and delocalized system is the intermolecular modes, they are shifted to lower energy because the intermolecular bonding in localized system is weaker. The bending modes remain roughly the same for localized, delocalized and vapor systems.

To understand how the directional feature of HBs depends on covalency, we look at the spacial distribution function of Oxygen atom, and the distribution of the H-O-O angle, shown in Fig 3.

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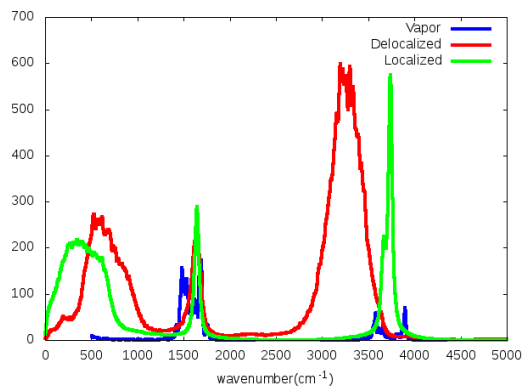


FIG. 2: IR spectrum. For water vapor, localized and delocalized systems. The low wavenumber part of the spectrum for vapor which corresponds to vibrational modes are not shown for simplicity. The O-H stretch mode ( $\sim 3600 \text{ cm}^{-1}$ ) for localized system is very similar to vapor which is none-interaction. And the intermolecular modes ( $\sim 500 \text{ cm}^{-1}$ ) moves to the left, indicating the intermolecular bonding is weaker.

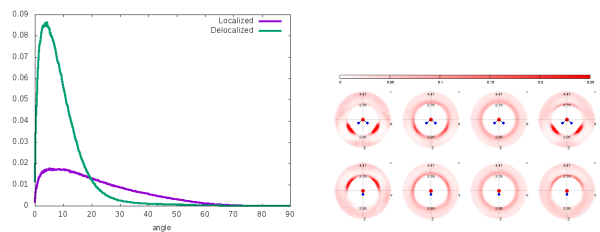


FIG. 3: angular and spacial distribution.

[1] E. Isaacs, A. Shukla, P. Platzman, D. Hamann, B. Barbiellini, and C. Tulk, Physical Review Letters **82**, 600

(1999).  
 [2] T. K. Ghanty, V. N. Staroverov, P. R. Koren, and E. R. Davidson, Journal of the American Chemical Society **122**, 1210 (2000).  
 [3] A. J. Stone, The Journal of Physical Chemistry A **121**, 1531 (2017).  
 [4] F. Weinhold, Encyclopedia of computational chemistry (1998).  
 [5] E. D. Glendening and A. Streitwieser, The Journal of chemical physics **100**, 2900 (1994).  
 [6] G. K. Schenter and E. D. Glendening, The Journal of Physical Chemistry **100**, 17152 (1996).  
 [7] E. D. Glendening, The Journal of Physical Chemistry A **109**, 11936 (2005).  
 [8] F. Weinhold, Advances in protein chemistry **72**, 121 (2005).  
 [9] K. Kitaura and K. Morokuma, International Journal of Quantum Chemistry **10**, 325 (1976).  
 [10] P. S. Bagus, K. Hermann, and C. W. Bauschlicher Jr, The Journal of chemical physics **80**, 4378 (1984).  
 [11] P. S. Bagus and F. Illas, The Journal of chemical physics **96**, 8962 (1992).  
 [12] W. J. Stevens and W. H. Fink, Chemical physics letters **139**, 15 (1987).  
 [13] W. Chen and M. S. Gordon, The Journal of Physical Chemistry **100**, 14316 (1996).  
 [14] Y. Mo, J. Gao, and S. D. Peyerimhoff, The Journal of

- Chemical Physics **112**, 5530 (2000).
- [15] A. J. Misquitta, B. Jeziorski, and K. Szalewicz, Physical review letters **91**, 033201 (2003).
- [16] R. Z. Khaliullin, E. A. Cobar, R. C. Lochan, A. T. Bell, and M. Head-Gordon, The Journal of Physical Chemistry A **111**, 8753 (2007).
- [17] J.-P. Piquemal, A. Marquez, O. Parisel, and C. Giessner-Prettre, Journal of computational chemistry **26**, 1052 (2005).
- [18] R. Z. Khaliullin, A. T. Bell, and M. Head-Gordon, Chemistry—A European Journal **15**, 851 (2009).
- [19] E. A. Cobar, P. R. Horn, R. G. Bergman, and M. Head-Gordon, Physical Chemistry Chemical Physics **14**, 15328 (2012).
- [20] R. Z. Khaliullin, J. VandeVondele, and J. Hutter, Journal of chemical theory and computation **9**, 4421 (2013).
- [21] R. Z. Khaliullin, M. Head-Gordon, and A. T. Bell, The Journal of chemical physics **124**, 204105 (2006).