Hydrogen-bond network and local structure of liquid water: An atoms-in-molecules perspective

Haigang Lu, Yuekui Wang, Yanbo Wu, Pin Yang, Lemin Li, and Sidian Li

---

Articles you may be interested in

Analysis of the basis set superposition error in molecular dynamics of hydrogen-bonded liquids: Application to methanol
J. Chem. Phys. **137**, 104506 (2012); 10.1063/1.4749929

Structural and atoms-in-molecules analysis of hydrogen-bond network around nitroxides in liquid water
J. Chem. Phys. **133**, 124508 (2010); 10.1063/1.3478999

Quantum effects of hydrogen atoms on the dynamical rearrangement of hydrogen-bond networks in liquid water
J. Chem. Phys. **132**, 164507 (2010); 10.1063/1.3397809

Relating linear vibrational spectroscopy to condensed-phase hydrogen-bonded structures: Liquid-to-supercritical water
J. Chem. Phys. **128**, 244510 (2008); 10.1063/1.2945896

Analysis of the hydrogen-bonded structure of water from ambient to supercritical conditions
J. Chem. Phys. **108**, 8528 (1998); 10.1063/1.476282

Hydrogen-bond network and local structure of liquid water: An atoms-in-molecules perspective

Haigang Lu,[1,a)] Yuekui Wang,[1] Yanbo Wu,[1] Pin Yang,[1] Lemin Li,[2] and Sidian Li[3]

[1]*Key Laboratory of Chemical Biology and Molecular Engineering of the Education Ministry, Institute of Molecular Science, Shanxi University, Taiyuan, Shanxi 030006, China*
[2]*College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China*
[3]*Xinzhou Teachers' University, Xinzhou, Shanxi 034000, China*

The nearly linear relationship between hydrogen-bond strength at the CCSD(T)/Aug-cc-pVTZ level and the electron density at the bond critical point in the atoms-in-molecules theory provides a practical means of calculating the hydrogen-bond strength in liquid water. A statistical analysis of the hydrogen-bonds obtained from Car-Parrinello molecular dynamics simulations shows that the strengths of hydrogen bonds in liquid water conform to a Gaussian distribution. Considering supercooled (250 K) water to have a fully coordinated (icelike) local tetrahedral configuration, we show that the local structure of liquid water is partly distorted tetrahedral in normal liquid water and even in superheated water. © *2008 American Institute of Physics.* [DOI: 10.1063/1.2985605]

I. INTRODUCTION

The hydrogen-bond (H-bond) network in liquid water is the key to describing its local structure and for understanding its unusual properties.[1–3] However, there are two controversial views concerning the H-bond network and therefore the local structure of liquid water: the traditional tetrahedral one is that, on average, each water molecule is H bonded to four nearest neighbors through two donor bonds and two acceptor bonds,[3–13] while the filamentous one is that, on average, each molecule only forms two strong H bonds, one acceptor and one donor bond.[14,15] The focus of controversy is the average number of H bonds per molecule calculated from experiments and molecular dynamics (MD) simulations.

Because of the random distribution of H bonds in liquid water, the H-bond number is highly dependent on the precise energetic,[3,16–18] geometric,[13,19–22] or electronic[11,13] definition. A comprehensive discussion of the different definitions can be found in Ref. 13. The geometric definition of a H-bond $(X\text{-}H\cdots Y)$ is straightforward and generally needs two parameters:[13] the distance $X\text{-}Y$ (or $H\text{-}Y$) and the angle $X\text{-}H\text{-}Y$. Therefore, it is complex to describe the statistical distribution of random H bonds. The energetic definition needs only one parameter: the H-bond strength of $H\cdots Y$. However, this can be neither experimentally measured nor directly calculated from the energy difference between the H-bond complex and its monomers in liquid water. In classical MD simulations, the H-bond strength is described by an empirical parameter: the effective pair potential between water molecules.[3] Recently, electronic definitions have been proposed based on Mulliken or Mayer bond orders[11] or the occupancy of the relevant antibonding $\sigma^*_{O\text{-}H}$ orbital in the natural bond orbital approach.[13,23]

The atoms-in-molecules (AIM) theory[24] is widely used to describe both covalent and H-bonding interactions. The AIM method uses the electron density as its starting point, which is a real object that can be obtained computationally or experimentally. In the topology of the electron density ρ, there are some critical points, i.e., the extrema of electron density where its gradient vector $\nabla\rho=0$. The critical point between two nuclei is called the bond critical point. In particular, an electron density in the range $0.002–0.035$ a.u. at the bond critical point has been proposed as a criterion of H-bond formation.[25] More interestingly, the H-bond strengths relate linearly to the electron densities at the H-bond critical points (ρ_{Hbcp}) of the AIM theory, from van der Waals interactions to classical H bonding to strong H bonding.[26]

Here, an AIM approach is used to calculate the H-bond strength in liquid water and provides an electronic and energetic definition of H bonds. For small water clusters, the H-bond strengths can be accurately calculated from high-accuracy *ab initio* calculations, for example, at the level of the coupled cluster method with single, double, and noniterative triple excitations [CCSD(T)].[27–31] Given the possible geometric structure of a H-bond complex, we can directly calculate the H-bond strengths from their ρ_{Hbcp} values. In liquid water, these required geometric configurations can be obtained from *ab initio* MD simulations, such as Car-Parrinello molecular dynamics (CPMD).[32,33] Consequently, the combination of these first principles calculations provides a practical means of calculating H-bond strengths and hence of investigating the random H-bond distribution in liquid water.

II. METHODS

There are three steps involved in calculating the H-bond strengths in liquid water: determination of the relationship between the H-bond strength and its ρ_{Hbcp}, establishment of the geometric configurations of liquid water, and evaluation of ρ_{Hbcp} values in liquid water.
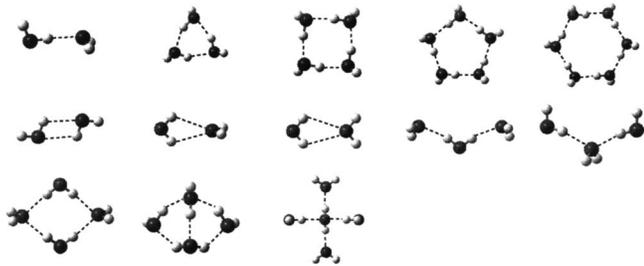
a)Electronic mail: luhg@sxu.edu.cn.

FIG. 1. The geometries and hydrogen bonds (dashed lines) of small water clusters. The black and white balls are oxygen and hydrogen atoms, respectively.

FIG. 2. The linear relationship between H-bond strength and its electron density (ρ_{Hbcp}) at the bond critical point of the AIM theory in some small water clusters. The a_0 is the Bohr radius.

First, we determined the relationship between the H-bond strength and its ρ_{Hbcp} using 13 small water clusters (Fig. 1). All molecular *ab initio* calculations were carried out using the GAUSSIAN 03 program.[34] The geometries of these small water clusters were optimized at the MP2/Aug-cc-pVTZ level, and their total energies were calculated at the CCSD(T)/Aug-cc-pVTZ level.[35] The H-bond strength (ΔE) was calculated using a supermolecule approach:

$$\Delta E = -(E_{\text{complex}} - nE_{\text{water}})/m, \qquad (1)$$

where E_{complex} and E_{water} are the total energies of the water cluster and the water molecule, and n and m are the total numbers of water molecules and of H bonds in the water cluster, respectively. The calculated ΔE values were corrected for basis set superposition error using the counterpoise method.[36]

The ρ_{Hbcp} values of the AIM method in the small water clusters were calculated both by means of the AIMPAC program[37] from the HF/Aug-cc-pVTZ wavefunction and by means of the "awk" program "WATER.AWK"[38] (written by us) from the "cube" (with mesh $128 \times 128 \times 128$) file of the total electron density in a cubic cell of 12.8 Å generated by the CPMD program.[39] A linear relationship was then fitted between ΔE and ρ_{Hbcp}.

In all CPMD calculations, the Becke-Lee-Yang-Parr (BLYP) gradient-corrected density-functional approach was adopted,[40,41] and the core-valence interactions were described by ultrasoft pseudopotentials (USPPs) for oxygen and hydrogen with a cutoff of 25 Ry.[42]

Second, we obtained the geometric configurations of liquid water by CPMD simulations performed on 65 water molecules in a cubic cell of 12.478 Å (density $\rho = 1.0$ g/cm^3) at 250, 300, 350, and 400 K, respectively. The initial configuration was obtained from classical MD after an equilibration period of 500 ps at 400 K. After initial wavefunction optimization, CPMD simulations were performed for 4.9 ps (50 000 steps). Temperature control during the simulation was accomplished with a Nosé–Hoover algorithm to keep the system in the so-called canonical ensemble (nVT ensemble).[43,44] A fictitious electron mass of 600 a.u. and a time step of 4.0 a.u. (0.097 fs) ensured good control of the conserved quantities.

After the CPMD simulations, we choose 1000 configurations between 40 000 and 50 000 steps to calculate the electron densities and the H-bond strengths in liquid water. Because, in accordance with the ergodic hypothesis (one of
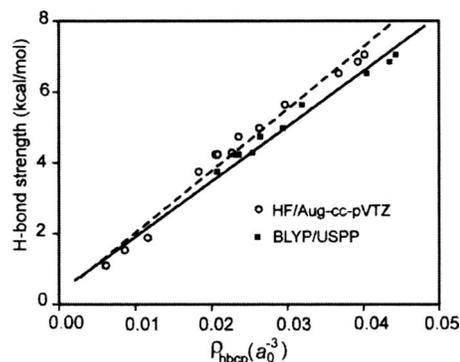
the fundamental axioms of statistical mechanics), the ensemble average is equal to the time averages, these 1000 configurations at different times should include most of the possible H-bond-coordinated structures of water molecules.

Thirdly, all possible H-bond strengths (ΔE) in these configurations were evaluated on the basis of the linear relationship with their ρ_{Hbcp} values. The possible O–H$\cdots$O H bonds were initially determined by considering two geometric criteria: the distance $R_{H\cdots O}$ being <3.0 Å and the angle $\angle$O–H$\cdots$O being $>90°$.[13] Between each proton and its acceptor, the electron densities at 100 equidistant points were evaluated from the cube files of the total electron density. The minimum of these densities in the bonding region corresponds to the ρ_{Hbcp} of the H bond.

III. RESULTS AND DISCUSSION

A. H-bond strength from AIM

From the *ab initio* calculations and AIM analyses of some small water clusters, the H-bond strength ΔE (kcal/mol) at the CCSD(T)/Aug-cc-pVTZ level is nearly linearly related to its ρ_{Hbcp} at the HF/Aug-cc-pVTZ or BLYP/USPP level, respectively (Fig. 2). The linear relationships are

$$\Delta E = 175.01\rho_{Hbcp} + 0.27 \quad (R = 0.989, \text{SD} = 0.30)$$

(at the HF/Aug-cc-pVTZ level) and

$$\Delta E = 156.14\rho_{Hbcp} + 0.35 \quad (R = 0.993, \text{SD} = 0.23)$$

(at the BLYP/USPP level), $\qquad (2)$

where R and SD are the correlation coefficient and the standard deviation of the linear fit, respectively. The nearly linear relationship (0.993) and the small standard deviation (± 0.23 kcal/mol) show that the O–H$\cdots$O H-bond strength can be accurately calculated from its electron density at the bond critical point.

Is this relationship applicable for H bonds in liquid water? The water clusters in the linear fit include not only global minimum configurations (the first row of Fig. 1) but also some local minima (the second and third rows in Fig. 1), which cover the majority of the H-bond-coordinated cases in liquid water, such as two-, three-, and four-coordinated mol-
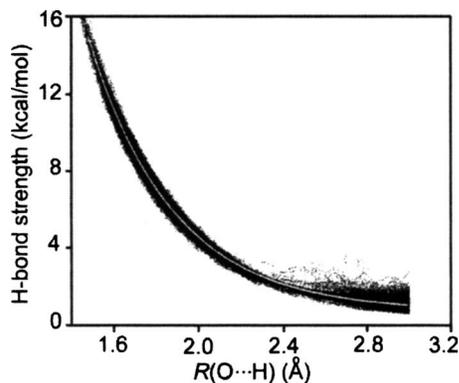
FIG. 3. The relationship between H-bond strength and the distance $R(H\cdots O)$ between the proton and its acceptor at 250 K. The white line is a fitted curve for exponential decay.

ecules. Consequently, this linear relationship is applicable for calculating the H-bond strength not only in water clusters but also in condensed water, such as ice and liquid water. For instance, the average H-bond strength (6.87 kcal/mol) from our AIM approach is only slightly greater than the experimental value (6.69 kcal/mol) in ice I_h.[45]

B. Gaussian distribution of H bonds in liquid water

In 1000 geometric configurations of a unit cell of 65 water molecules, there are more than 150 000 possible H bonds at 250, 300, 350, and 400 K, respectively, the strengths of which range from 1.0 to 16.0 kcal/mol. Obviously, there are many strong H bonds (>8.0 kcal/mol) beyond the range of the linear fit. The question then arises as to whether these strong H bonds can be reliably calculated by the linear relationship of the AIM approach. As shown in Ref. 30, the H-bond strength increases approximately linearly with its ρ_{Hbcp} on going from weak H bonds to moderate and strong H bonds. In particular, the strength of this strong H bond decays exponentially (correlation coefficient: 0.993) with the distance between the acceptor and proton over the whole range of 1.0–16.0 kcal/mol (Fig. 3). Consequently, it is safe to conclude that all of these H bonds in liquid water are reliably indicated by their ρ_{Hbcp} values.

By frequency count with a step size of 0.10 kcal/mol, the strengths of these possible H bonds form two peaks at each temperature (250, 300, 350, and 400 K, Fig. 4), where the strong and weak peaks correspond to hydrogen bonding and weak interactions (including weak hydrogen bonding and van der Waals interactions), respectively. As the temperature is increased, the hydrogen bonding in liquid water becomes weak and disperses to gradually approximate the weak interactions, which is qualitatively consistent with the conclusion of the effective molecular pair interaction from the classical MD simulation.[3] Only at 250, 300, and 350 K are there clear gaps between the peaks of hydrogen bonding and weak interactions (Fig. 4).

Statistical analysis shows that the H-bond strengths conform to a Gaussian distribution in liquid water. The strong peak, separated by the minimum of a curve between the two peaks, may be fitted by a Gaussian function:
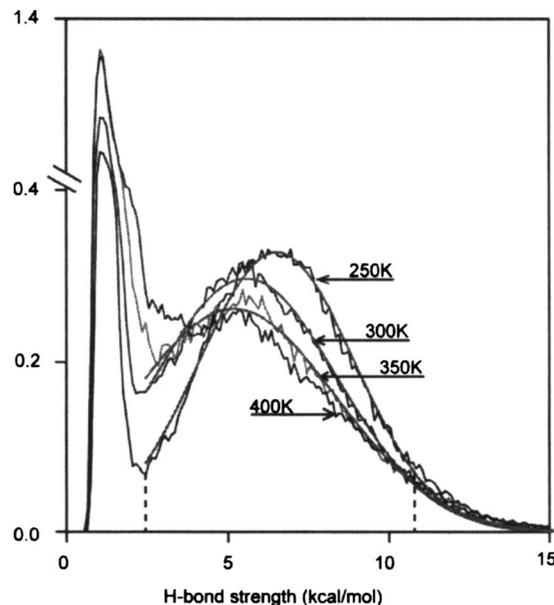

FIG. 4. The distributions of H-bond strengths in liquid water at different temperatures. The part of the y axis above 0.40 is reduced to one-fifth for completeness of the graph.

$$y = \frac{A}{\sigma\sqrt{2\pi}} \exp\left(-\frac{(x-x_c)^2}{2\sigma^2}\right), \qquad (3)$$

where x_c and σ are the mean and standard deviation, respectively, and A is the average area of a water molecule under the Gaussian curve. The high correlation coefficient of the determination ($R^2 > 0.995$, Table I) using a Gaussian fit shows that the H-bond strengths do indeed conform to a Gaussian distribution in liquid water. This conclusion is to be expected because the Gaussian distribution gives the maximum entropy subject to the condition that the standard deviation of x is fixed at σ. Due to the existence of weak interactions in liquid water, however, the Gaussian distribution is nearly perfect in supercooled water (250 K), approximate in normal liquid water (300 and 350 K), and destroyed in superheated water (400 K).

The Gaussian distribution of bond strengths in liquid water provides a quantitative approach for describing the properties of the H-bond network. As the temperature is increased from 250–350 K, the mean H-bond strength is gradually reduced from 6.51–5.18 kcal/mol, and the respective dispersions (indicated by the standard deviations) increase from 2.44–3.20 kcal/mol. Eventually, at 400 K, the peak due to

TABLE I. Gaussian parameters of distributions of H-bond strengths. (T indicates the temperature of liquid water or the structure of water, x_c and σ are its mean and standard deviation, A is the average area of a water molecule under the Gaussian curve, and R^2 is the correlation coefficient of the determination by a Gaussian fit.)

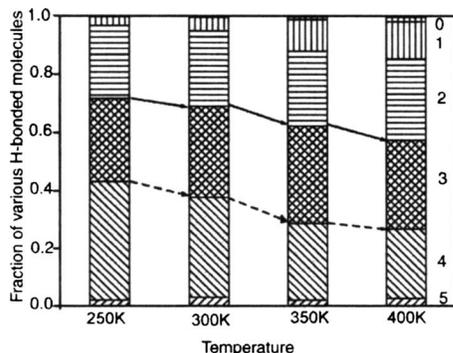| T	x_c (kcal/mol)	σ (kcal/mol)	A	R^2
Ice I_h	6.87			
Cubic ice	6.46			
250 K	6.51	2.44	2.00	0.995
300 K	5.56	2.87	2.13	0.997
350 K	5.18	3.20	2.09	0.996

FIG. 5. Fraction of molecules bonded by various numbers (numbers at the right-hand side) of H bonds in liquid water at 250, 300, 350, and 400 K, respectively.

hydrogen bonding almost disappears. Here, we can use the Shannon entropy[46] $H=\log[(2\pi e)^{1/2}\sigma]$ to describe the relative disorder of the H-bond network. Thus, as the temperature of liquid water is increased from 250 – 350 K, the relative increase in the Shannon entropy of the H bonds is from log 2.44 to log 3.20.

C. Local structure of liquid water

The Gaussian distribution of H-bond strengths provides an approach for investigating the local structure and H-bond network of liquid water. In particular, in supercooled water (250 K), the Gaussian distribution of H-bond strengths is approximately perfect and its mean (6.51 kcal/mol) lies between the H-bond strength of cubic ice (6.46 kcal/mol) and that of ice I_h (6.87 kcal/mol), which are two perfect tetrahedral structures. Therefore, it is safe to conclude that the local structure in this supercooled water is approximately tetrahedral, as was assumed in Ref. 4. This conclusion provides a natural benchmark for describing the relative distortion of the local tetrahedral structure in liquid water at other temperatures. Because H bonds that are either too weak or too strong will lead to destruction of the local tetrahedral structure, we choose the energetic cutoff of 6.51 ± 4.11 kcal/mol (between the two dashed lines in Fig. 4), where the lower limit of 2.40 kcal/mol corresponds to the strength of the minimum between the two peaks.

At the four temperatures of 250, 300, 350, and 400 K, the average numbers of H bonds between the energetic cutoffs are 3.6, 3.5, 3.2, and 3.16, respectively, which indicates that liquid water should be locally tetrahedral at normal temperatures. To describe the detailed local coordinated case of molecules in a liquid, we define water molecules with four, three or five, and less than three H bonds as tetrahedral, distorted tetrahedral, and destroyed tetrahedral, respectively. In the case of supercooled water (250 K), 41% of the molecules are tetrahedral, so that this is the main local structure of the liquid. Therefore, it is reasonable to choose it as a benchmark for describing the local structure. At 300, 350, and 400 K, there are 35, 27, and 24% tetrahedrally coordinated molecules, respectively (Fig. 5, dashed arrows). Thus, at 300 K, the tetrahedral molecules are still the predominant component (35%), while at 350 and 400 K, the distorted tetrahedral molecules are more prevalent. Taking the tetrahe-

dral and distorted tetrahedral molecules as a whole, these account for about 72, 69, 62, and 57% of the molecules at the four respective temperatures (Fig. 5, solid arrows). That is to say, the principal local structures in liquid water are partly distorted in supercooled, normal, and even superheated liquid water. This conclusion supports the classical picture of liquid water, in which each molecule is mainly tetrahedrally coordinated rather than the lower coordinated filamentous geometry.

IV. CONCLUSION

In this paper, we have provided an AIM perspective on the hydrogen-bond network and the local structure of liquid water. The key is the nearly linear relationship between the hydrogen-bond strength at the CCSD(T)/Aug-cc-pVTZ level and the electron density at the bond critical point in the AIM theory, which has been determined from some small water clusters. This linear relationship provides a simple means of calculating H-bond strengths in liquid water.

After a statistical analysis of H bonds obtained from CPMD simulations at 250, 300, 350, and 400 K, we obtained a quantitative statistical description of the Gaussian distribution of H-bond strengths. The Gaussian distribution at 250 K provides a natural benchmark for the local tetrahedral structure of liquid water, which shows that, in contrast to the tetrahedral structure of ice, the local structures are partly distorted tetrahedral in liquid water. This AIM approach may also be used to investigate hydrogen bonds at interfaces between liquid water and air or hydrophobic materials.

[1] *Water: A Comprehensive Treatise*, edited by F. Franks (Plenum, New York, 1972), Vol. 1.
[2] F. Franks, *Water* (Royal Society of Chemistry, Cambridge, 1983).
[3] F. H. Stillinger, Science **209**, 451 (1980).
[4] J. D. Smith, C. D. Cappa, K. R. Wilson, B. M. Messer, R. C. Cohen, and R. J. Saykally, Science **306**, 851 (2004).
[5] T. Head-Gordon and M. E. Johnson, Proc. Natl. Acad. Sci. U.S.A. **103**, 7973 (2005).
[6] R. Bukowski, K. Szalewicz, G. C. Groenenboom, and A. v. d. Avoird, Science **315**, 1249 (2007).
[7] J. M. Sorenson, G. Hura, R. M. Glaeser, and T. Head-Gordon, J. Chem. Phys. **113**, 9149 (2000).
[8] A. K. Soper, Chem. Phys. **258**, 121 (2000).
[9] G. W. Robinson, S.-B. Zhu, S. Singh, and M. W. Evans, *Water in Biology, Chemistry and Physics* (World Scientific, Singapore, 1996).
[10] M. V. Fernandez-Serra and E. Artacho, J. Chem. Phys. **121**, 11136 (2004).
[11] M. V. Fernandez-Serra and E. Artacho, Phys. Rev. Lett. **96**, 016404 (2006).
[12] M. Leetmaa, M. Ljungberg, H. Ogasawara, M. Odelius, L. A. Naslund, A. Nilsson, and L. G. M. Pettersson, J. Chem. Phys. **125**, 244510 (2006).
[13] R. Kumar, J. R. Schmidt, and J. L. Skinner, J. Chem. Phys. **126**, 204107 (2007).
[14] Ph. Wernet, D. Nordlund, U. Bergmann, M. Cavalleri, M. Odelius, H. Ogasawara, L. Å. Näslund, T. K. Hirsch, L. Ojamäe, P. Glatzel, L. G. M. Pettersson, and A. Nilsson, Science **304**, 995 (2004).
[15] L.-Å. Näslund, J. Lüning, Y. Ufuktepe, H. Ogasawara, P. Wernet, U. Bergmann, L. G. M. Pettersson, and A. Nilsson, J. Phys. Chem. B **109**, 13835 (2005).
[16] W. L. Jorgensen, J. Chandrasekhar, J. D. Madura, R. W. Impey, and M. L. Klein, J. Chem. Phys. **79**, 926 (1983).
[17] A. Geiger and H. E. Stanley, Phys. Rev. Lett. **49**, 1749 (1982).
[18] H. E. Stanley and J. Teixeira, J. Chem. Phys. **73**, 3404 (1980).
[19] I. W. Kuo and C. J. Mundy, Science **303**, 658 (2004).
[20] B. Hetenyi, F. De Angelis, P. Giannozzi, and R. Car, J. Chem. Phys. **120**, 8632 (2004).

[21] A. Luzar and D. Chandler, J. Chem. Phys. **98**, 8160 (1993).

[22] A. D. Hammerich and V. Buch, J. Chem. Phys. **128**, 111101 (2008).

[23] F. Weinhold and C. Landis, *Valency and Bonding: A Natural Bond Orbital Donor-Acceptor Perspective* (Cambridge University Press, Cambridge, 2005).

[24] R. F. W. Bader, *Atoms in Molecules: A Quantum Theory* (Clarendon, Oxford, UK, 1990).

[25] U. Koch and P. Popelier, J. Phys. Chem. **99**, 9747 (1995).

[26] R. Parthasarathi, V. Subramanian, and N. Sathyamurthy, J. Phys. Chem. A **110**, 3349 (2006).

[27] J. Cizek, Adv. Chem. Phys. **14**, 35 (1969).

[28] G. D. Purvis and R. J. Bartlett, J. Chem. Phys. **76**, 1910 (1982).

[29] G. E. Scuseria, C. L. Janssen, and H. F. Schaefer III, J. Chem. Phys. **89**, 7382 (1988).

[30] G. E. Scuseria and H. F. Schaefer III, J. Chem. Phys. **90**, 3700 (1989).

[31] J. A. Pople, M. Head-Gordon, and K. Raghavachari, J. Chem. Phys. **87**, 5968 (1987).

[32] R. Car and M. Parrinello, Phys. Rev. Lett. **55**, 2471 (1985).

[33] J. VandeVondele, F. Mohamed, M. Krack, J. Hutter, M. Sprik, and M. Parrinello, J. Chem. Phys. **122**, 14515 (2005).

[34] M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, GAUSSIAN 03, Revision E.01, Gaussian, Inc., Wallingford CT, 2004.

[35] R. A. Kendall, Jr., T. H. Dunning, and R. J. Harrison, J. Chem. Phys. **96**, 6796 (1992).

[36] S. F. Boys and F. Bernardi, Mol. Phys. **19**, 553 (1970).

[37] AIMPAC (http://www.chemistry.mcmaster.ca/aimpac/).

[38] See http://faculty.sxu.cn/luhg/water.txt.

[39] CPMD code, Version 3.11.1, Copyright IBM Corp. 1990–2006, Copyright MPI für Festkörperforschung Stuttgart, 1997–2001.

[40] A. D. Becke, Phys. Rev. A **38**, 3098 (1988).

[41] C. T. Lee, W. Yang, and R. G. Parr, Phys. Rev. B **37**, 785 (1988).

[42] K. Laasonen, A. Pasquarello, R. Car, C. Lee, and D. Vanderbilt, Phys. Rev. B **47**, 10142 (1993).

[43] S. Nosé, J. Chem. Phys. **81**, 511 (1984).

[44] W. G. Hoover, Phys. Rev. A **31**, 1695 (1985).

[45] E. Whalley, Trans. Faraday Soc. **53**, 1578 (1957).

[46] C. E. Shannon, Bell Syst. Tech. J. **27**, 379 (1948).